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The distribution of halogens in skarn amphiboles in Central Sweden

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ABSTRACT

Determinations of halogens in paragenetically well-defined skarn amphiboles in the Precambrian of Central Sweden have hitherto been very scarce. New data, 23 on fluorine and 10 on chlorine, with 5, respectively 2, old ones (table p. 497) show that F ranges from 0.07 to 2.34 per cent, while Cl in amphiboles with only bivalent cations shows a maximum figure of only 0.037 per cent but in one common hornblende is 0.20 and in a ferrohastingsite 1.42 per cent. In pyrometasomatic deposits the amount of F in the amphiboles appears to show a very rough proportion to the occurrence of more fluorine-rich minerals in the paragenesis, as humites. In this group there is practically no Cl. Occurrences of amphiboles previously designated as "reaction skarns" and interpreted as originated through interior reactions in ore deposits subjected to regional heating, contain F in amounts comparable to those in the pyrometasomatic skarns.

All the examined occurrences have got their present mineralogical and textural characters when the containing surficial leptite formation was subjected to metamorphism in connexion with the intrusion of the earlier group of Svionian granites and the contemporaneous metasomatic action designated as "the magnesia metasomatism". The analytical results indicate that the agents of this metasomatism, whose action appears to have been in part pyrometasomatic, in part hydrothermal in nature, have introduced much more fluorine than has previously been assumed. Three point samples of mica schists derived from the alteration of leptites indicate that in these rocks, quantitatively the chief products of the metasomatism in question, fluorine has been introduced in amounts comparable to those recorded in hydrothermal sericitization. Concerning the amount of chlorine no conclusion is possible but the total lack of scapolite in the parageneses may be an indication that it was more subordinate. Further, the data on fluorine in the "reaction skarns" call for a certain revision of the earlier interpretation of these skarns as far as such of amphiboles are concerned.

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Introduction

Although it has long been known that fluorine may enter into the amphibole structure, knowledge of its occurrence in this mineral group is still unsatisfactory in several respects. Many older analyses have omitted the determination of fluorine, probably because the methods then available were found cumbersome. Also, as will be seen from the following, there is reason to suspect that the figure for fluorine, when thus determined, may sometimes be radically wrong also in otherwise reliable analyses.¹ Chlorine as a constituent of amphiboles has received still less attention. Although some remarkable cases were reported, as the dashkesanite of Krutov (1936), current opinion on the subject even a few years ago is reflected in Goldschmidt's "Geochemistry", published posthumously in 1954 (p. 586): "we never observe the presence of chlorine in such hydrosilicates as the micas, amphiboles, or humites, into which fluorine enters very freely". But recent studies indicate that it may occur in amounts quite comparable to those of fluorine (e.g. Buddington and Leonard 1953).

From the amphiboles that occur as gangue minerals in many ore deposits of the Precambrian of Central Sweden, both sulfide and magnetite ores, data on halogens have been much too few to give an idea of the role of these elements in the geochemical processes that have been active in their formation. Better analytical methods now offer an opportunity to fill this gap in our knowledge of the geological history of the ore deposits in question.

Of the other fluorine-bearing silicates that occur in these deposits, those of the humite group are fairly well known. The extremely few data available on fluorine in the skarn micas indicate that also this mineral group may carry considerable amounts of it. But micas are, quantitatively, much less important as skarn minerals than the amphiboles, and this study has been restricted to the latter. As to chlorine, the parageneses in question do not include any mineral that regularly contains it. But in some deposits, scapolite occurs as manifestly belonging to a paragenesis connected with distinctly later geological events.

It has not been possible to obtain complete amphibole analyses to the number required to get a general idea of the distribution of the halogens. Nor have such analyses been necessary for the geochemical purpose of this investigation; optical determinations sufficient to identify the species have been enough in most cases.² On the other hand, it has been of the greatest importance to select for analysis amphiboles of such known geological relations that conclusions may reasonably be extended beyond the individual specimen. Most of the material has been chosen from deposits with which the writer himself is familiar, and among specimens collected by him. For similar reasons, there is here given not only a general picture of the geological setting of the different types of amphibole occurrences, but also brief characteristics of the various deposits. Certain textural variations will also be described and discussed, as they may throw some light upon the formation process of the skarn amphiboles.

¹ This view has already been expressed by Rankama and Sahama (1950, p. 760), who write "Many of the earlier determinations are unreliable, and new determinations by modern methods are few."

² The somewhat arbitrary limit between tremolite and actinolite has been so placed that the latter term embraces those members of the series that show a distinct colour in a thin section of ordinary thickness.

Beside the new data, there are given also all earlier determinations, when the paragenetical relations of the amphibole are sufficiently well known.

The analytical chemical work on which this study rests, has been done by Mr. Alexander Parwel, of the Mineralogical Department of the Swedish Museum of Natural History. The writer also wishes to express his gratitude for the aid extended to him by Professor F. E. Wickman, Curator of the Department, who has put its resources at the writer's disposal, and to Professor N. H. Magnusson, formerly director of Sveriges Geologiska Undersökning, for the opportunity to select, from the stored and registered collections of that institution, most of the material to be analysed.

Separation of material for analysis was made by the usual methods of magnetic separation, heavy liquids, and picking under a binocular microscope. While the product was, in all cases, free from any admixture of other minerals that might contain halogens, several samples had to be accepted although containing a few percent of other impurities, as diopside, since this did not materially affect the results, considering the aim of the study.

As to the analytical methods employed, Mr. Parwel has communicated the following:

Determination of fluorine.—The fluorine was separated by distillation and its quantity determined by titration. The following technique was employed.

The pulverised mineral sample which ought to contain 1–10 mg F, was fused with ca 5 times its weight of NaOH, in a silver crucible. The melt was leached and transferred to a platinum dish. Excess NaOH was neutralized with H_2SO_4 until the solution became weakly alkaline. The solution (incl. precipitate) was evaporated to about 15–20 ml volume and transferred to the apparatus for the distillation of HF described by Huckaby, Welch, and Melter (1947). Now were added 20 ml H_2SO_4 , and distillation was carried out at $146^\circ C$; 200 ml distillate were collected.

The distillate was transferred to a platinum dish, and NaOH added until the reaction became weakly alkaline, whereupon it was evaporated to ca 5 ml volume. Distillation at $146^\circ C$ was repeated, and 100 ml distillate were collected in a volumetric flask.

If the sample contained but little F the whole distillate was neutralized to a weakly alkaline reaction and evaporated to 25 ml (Note: blank runs are prepared in the same way). To the solution were added 4 drops alizarin S (0.05 percent), whereafter it was neutralized with 0.05 N HCl. To this solution (25 ml) were added 25 ml ethyl alcohol (96 percent) and 1 ml monochloroacetic acid as a buffer solution, giving a pH of 3.3–3.4.

The buffer solution was made from 21 g monochloroacetic acid and 3 g NaOH in 100 ml water. It must not be older than 2 weeks and was often controlled by determining pH in a sample solution exactly corresponding to the one used as above.

At titration, pH changes with the concentration of alcohol. Therefore the $Th(NO_3)_4$ solution was so made that it had the same alcohol concentration as the sample solution. A 0.01 N $Th(NO_3)_4$ solution was used. The amounts of fluorine were so chosen that the consumption of titration solution did not exceed 10 ml, that is, the maximum final volume was 60 ml.

To eliminate possible distillation and titration errors an empirical curve was employed. A synthetic mixture free from fluorine but otherwise with the same composition as the sample was decomposed. Known amounts of fluorine were added, and a series of samples were distilled and treated in exactly the same way as the mineral samples, and were titrated with the same $Th(NO_3)_4$ solution. From the empirical curve all fluorine percentages in the mineral samples were calculated.

The chemicals may contain a little fluorine. Further, traces of H_2SO_4 may distill over and cause a certain consumption of $\text{Th}(\text{NO}_3)_4$. Therefore one must always carry out blank runs that are made in every detail like the determinations on mineral samples. The amounts obtained are subtracted from the values obtained for the latter. In the present work, about each fifth run has been a blank.

Determination of chlorine.—The mineral samples in which chlorine was to be determined contained only small amounts of it. It was therefore advisable first to separate the chlorine from the other constituents that might interfere with its determination. Because of the good results obtained by using the distillation method for fluorine, a similar procedure for chlorine was studied. It was found that one could distill over chlorine quantitatively, and after trying several variations of the method the following one was decided upon. With a chlorine percentage between 0.001 and 0.2, which was the common case, 0.7–1.0 g of the sample was fused with 5 times its weight of NaOH, using a nickel crucible. The melt was leached with water, and generally there was added 1 ml 0.02 *N* NaCl solution (compare below for motive). The solution was neutralized with concentrated H_2SO_4 to weakly alkaline reaction, and after evaporation to about 20–30 ml volume it was transferred to the distillation apparatus. The latter was of the same construction as that used in the determination of fluorine (compare above), only that the interior volume was greater (about 280 ml) because of the greater samples.

Now were added 20 ml concentrated H_2SO_4 , distillation was made at 146°C, and 200 ml distillate were collected. This was placed in a platinum dish and neutralized with NaOH to weakly alkaline reaction, and then evaporated to a volume of 3–5 ml. Thereafter a second distillation was carried out, but it proved advantageous to do this in series, of 4 samples and one blank run each. In the smaller distillation apparatus were put 10 ml concentrated H_2SO_4 , and a blank run with water vapour was made (about 100 ml distillate) in order to drive off possible chlorine from the H_2SO_4 .¹ This acid had not to be changed during the running of the series. The solution of 3–5 ml was now transferred to the distillation apparatus and distillation carried out at 137–138°C (metaxylol being used instead of tetrachlorethane) as a higher temperature was not required; 100 ml distillate were collected.

The distillate was placed in a platinum dish and evaporated to half its volume in order to get rid of most of the CO_2 , whereupon the solution was neutralized with some drops of HAc and evaporated to a small volume. It was then transferred to a 10 ml Erlenmeyer flask and, after some drops of HAc had been added, evaporated on a steam bath to dryness. This was done because it is important that all CO_2 is eliminated; one may even have to add HAc once more, and evaporate. The rest was dissolved in 1 ml water, and the solution's pH carefully adjusted to 6.5–6.8 with the aid of HAc and NaAc buffer solution. Now were added 2 ml acetone and one drop 0.02 per cent dichlorofluorescein as indicator, and chlorine titrated with a 0.02 *N* AgNO_3 solution (2 ml microburette) according to Bullock and Kirk (1937).

The blank sample consisted of a synthetic chlorine-free mixture fused with NaOH, to which was added 1 ml 0.02 *N* NaCl solution. The chlorine figure from the blank run was subtracted from the result obtained from the mineral sample.

In the first apparatus the sulfuric acid had to be changed each time, and the apparatus had to be cleaned from precipitates. The reason for adding NaCl to the

¹ This must also be done at the first distillation, if the H_2SO_4 used should not be free from chlorine.

sample is that a distinct change of colour at titration can be observed only if the quantity of chlorine exceeds 0.2 mg. If one knows in advance that so must be the case, addition of NaCl is therefore unnecessary."

Geological orientation

The ore deposits, the amphiboles of which form the subject of this investigation, all belong to the Svionian, the oldest known division of the Swedish Precambrian.¹ They occur in rocks of the leptite formation: metamorphic, generally siliceous volcanics (leptites) and intercalated beds of limestone and dolomite. Also genetically belonging to this formation are—beside the "apatite iron ores" which fall outside the scope of this study—very numerous deposits of iron ore that originated through chemical sedimentation or, more rarely, through replacement at comparatively low temperatures. During the subsequent intense folding of this surficial formation there rose into it the huge concordant intrusions of the Earlier group of Svionian granites. This magmatic invasion was accompanied by the introduction of emanations (presumably in part gaseous, in part hydrothermal solutions) which brought about extensive chemical and mineralogical changes within the older formation. Because of the conspicuous role of magnesium among the substances that were thus introduced, the process is spoken of as "the magnesia metasomatism". The majority of the sulfide ore deposits of the region were formed in this way, and also a number of pyrometasomatic iron ore deposits. In the earlier formed iron ores, new mineral assemblages developed where originally both carbonates and quartz had been present. It has been assumed that these interior reactions were caused by regional heating alone, and the products are called "reaction skarn ores", in contrast to the "primary skarn ores" of pyrometasomatic origin. Furthermore, the magnesia metasomatism has often produced radical changes in these reaction skarns, frequently as to obliterate almost all traces of their earlier nature which can only be inferred from a comparison with less affected occurrences.

The sulfide deposits occur both in the carbonate rocks and in the siliceous volcanics. In the former, most occurrences are clearly of the pyrometasomatic type. Amphiboles are the most common accompanying skarn silicates, but diopside predominates in several deposits, and andradite garnet in a few others. Of the different kinds of amphibole, tremolite is most common; further there is actinolite and anthophyllite and, less frequently, hornblende and cummingtonite. With the amphiboles, minerals of the humite group are generally present. In the siliceous country rock, sulfide mineralization by replacement has been accompanied by an intense and often very wide-spread alteration, culminating in the development of rocks composed of quartz and silicates of Mg, Fe, and Al, such as cordierite, andalusite, anthophyllite, and biotite. In the Falun mine such rocks have long been known as quartzite, and this term will, for lack of a better one, be used here, although with quotation marks to emphasize that it is not a quartzite in the ordinary meaning of that term.

The skarns associated with iron ores present a more complicated problem. Also,

¹ Several Fennoscandian geologists use the term Svecofennian, originally introduced to designate the Precambrian orogenic zone of Central Sweden and southwestern Finland, also for the unit of geological time represented by the rocks of this zone, thus synonymously with Svionian. Since this differs from common usage in geological nomenclature, and may lead to confusion, the writer prefers to employ the clearly defined term Svionian for the time unit.

in their case the results of this study give more information of interest. The present state of our knowledge of this group may be summarized as follows.¹

The magnetite ores interpreted as being of pyrometasomatic origin, in their typical development are accompanied by the same skarn silicates as the sulfide deposits in carbonate rocks. Thus the combination of tremolite and humite minerals is common. A more basic and pronouncedly magnesian variety is characterized by chondrodite and forsterite, sometimes borates, chiefly ludwigite, and spinel (Geijer 1939). There exist transitional forms between this type and that with tremolite and humite minerals. Also low-iron diopside may be found in some quantity in both associations, while andradite is rare. When alone forming the skarn, diopside and andradite are not diagnostically decisive as they also, and very frequently, occur as chief constituents of reaction skarns; in the latter, the diopside is generally more ferri-ferous (hedenbergitic). Fluorite, which occurs in many of the pyrometasomatic sulfide deposits, is extremely rare as a primary constituent of a magnetite deposit, although deposition of fluorite with iron in the form of silicate (andradite) has been a characteristic feature in the formation of several sulfide ores (Geijer 1917, 1936, 1958).

The rather rare Källfall type of magnetite ore, represented mainly in the Riddarhyttan district (Geijer 1923), presents a special problem. The proportion of magnetite to skarn is higher than is generally the case in the skarn ores of the region. The chief gangue mineral is anthophyllite, more subordinate are cordierite, quartz, and biotite. Thus the nature of the gangue is the same as in many of the sulfide ores of the region. Likewise the leptite wall rock shows alteration of exactly the same character as that accompanying these sulfide deposits. It seems natural, then, to ascribe to the Källfall type the same origin by replacement in siliceous rocks. The problem is not so simple, however, for there are known cases where quartz-banded sedimentary iron ores have been affected by the magnesia metasomatism and altered in a direction towards the mineral assemblage of the Källfall type. On the other hand, this type proper exhibits some features that appear to distinguish it from these products of the alteration of quartz-banded ores, as its higher proportion of iron to silica, and lower phosphorus. Also small occurrences of "model size", with their surrounding halo of alteration, are known, whose characters seem incompatible with an origin through alteration of pre-existing sedimentary ores (Geijer 1923, p. 68 and 87). With our present knowledge of the Källfall type, one cannot get beyond this statement of the problem.

The development of skarns through reactions that were isochemical (apart from the loss of CO_2) has been very clearly demonstrated for several types of iron ores in the region. The probability of such reactions was first pointed out in discussing the manganiferous iron ores in dolomite or limestone (Lindroth 1919). These ores, with several per cent manganese, originally consisted of an iron-manganese carbonate which is still preserved in some deposits, and some quartz (about 3–20 per cent). Several occurrences exhibit a quite regular bedding, indicating sedimentary deposition. Others show replacement relations and apparently accompanying dolomitization, and seem to have been originally analogous to the carbonatic Bilbao type of replacement iron deposits. Metamorphism has produced magnetite and a number of manganiferous skarn silicates, chiefly of the olivine, garnet, and cummingtonite-grunerite series, the latter now frequently designated by the group name dannemonte. The silica that entered into these minerals was derived from the original quartz

¹ This summary is based on a joint publication by N. H. Magnusson and the present writer (Geijer och Magnusson 1944, summarized in 1952a and 1952b).

and also in part from adjacent siliceous rocks, as layers of lepidolite interstratified with the dolomite or limestone. Thus typical "boundary" skarns developed where the carbonatic ore was in contact with such rocks.

In the quartz-banded ores—a common type in the region—andalusite garnet, diopside (mostly hedenbergitic), and actinolite frequently occur as subordinate constituents. Their origin has been ascribed to reactions between iron minerals (as hematite), quartz, and limestone or dolomite seams, but considerable movement of material must have taken place to result in the present distribution of the skarn minerals. Sometimes whole beds are thus transformed into skarn masses with magnetite and enclosing unaltered lumps of quartz-banded ore. A good example has been described from the neighbourhood of the small mine Konstgruvan in Norberg (Geijer 1936). That such processes may result in typical skarn ore bodies has been shown most convincingly (compare especially Magnusson 1940). Very many skarn ore occurrences with a more or less distinct bedding, and with a gangue of actinolite, hornblende, diopside or andradite, comprising the majority of the non-manganiferous skarn ore deposits of the region, have been interpreted in this way.

Further, Magnusson (1930) has demonstrated that the massive hematite-quartz ores in dolomite at Långban have been partly transformed into magnetite ore with skarn, and the associated manganese ores correspondingly altered. The Långban deposits present special geochemical problems, however, and have not been included in this investigation.

Of great importance for the interpretation of the non-manganiferous skarn ores in general have been Magnusson's observations in the Persberg and Nordmark districts (Magnusson 1925, 1929) that pronouncedly magnesian skarns, whose characters indicate their connexion with the magnesia metasomatism, replace earlier formed andradite-diopside skarns which are by him interpreted as results of isochemical reactions.

The amphibole samples now analysed for halogens have been selected so as to cover, as completely as has been possible with the available number of analyses, the various types of skarn as described above.

The textural development of the different kinds of skarn amphiboles presents some characteristic features that deserve to be mentioned in this connexion, although they seem in part impossible to explain at present. Generally it is not a question of invariable rules but of the common occurrence, in some varieties or parageneses, of textures that are much rarer in others. It is, of course, impossible to give any statistical figures, but the different frequency of the various forms of growth is a trait that thrusts itself upon the observer.

All the kinds of amphiboles may occur as scattered metasomes with a more or less pronounced prismatic habit. The anthophyllite, however, shows this development only in a few cases, as in the quartziferous pyrite ore of the Falun mine, and in the magnetite ore of the Alabama ore body at Persberg; both occurrences will be described in the following. It is probable also that the first stage in the replacement of a carbonate rock by anthophyllite takes this form, although it is doubtful whether it is anywhere preserved as such. But in the quantitatively most important occurrences, the cordierite-anthophyllite "quartzites", this textural form is never encountered.

Skarn aggregates of amphiboles generally are built up of such stalks, arranged more or less at random. As to other textures, the calciferous monoclinic amphiboles exhibit the following characteristics. In tremolite the stalks very often start from a common point, forming radiating sheaves or regular stellate aggregates. Actinolite,

again, appears to show such growths less frequently. Also hornblende is not so often seen in any form of radiating texture, and its stalks are frequently shorter.

Among the orthorhombic amphiboles anthophyllite, when replacing carbonate rocks, shows very much the same textural features as the tremolite. In all the forms of "quartzites" originated through the alteration of leptytes, on the other hand, it exhibits another and most characteristic texture, forming stellate groups of fine needles, very regular in the plane of schistosity but showing, at the centre, almost no growth perpendicular to that direction. This, with two insignificant exceptions, holds true not only of the anthophyllite *sensu stricto* but also of the much less common gedrite that is met with in some more iron-rich "quartzite" varieties. One exception is found in the Falun mine. Its small bodies of gold ore are phases of the "quartzite" very poor in silicates, these being represented only by very small, rounded grains of anthophyllite (Törnebohm 1893). The other exception has been noted at Väster-Silvberg where a local form of "quartzite" is made up of quartz, almandite garnet, staurolite, and gedrite, the latter occurring as separate prismatic grains (Geijer 1917).

The non-manganiferous members of the monoclinic cummingtonite-grunerite series have, as far as the writer can recall, never been found as radiating aggregates. It is worth mentioning that there has been observed in the Falun mine a cordierite-bearing "quartzite" with cummingtonite instead of the usual anthophyllite; in this case, too, the monoclinic amphibole forms separate stalks. In the manganiferous members of the series (dannemorites) which only occur in reaction skarns, radiating growths appear to be very rare, but occasionally even a tendency to stellate grouping has been observed.

The factors that cause the development of radiating growths of amphiboles in replacement, instead of separate metasomes, are unknown, as they are in the similar case of tourmaline, for example. Although no explanation can be offered on this point, some other aspects of the textural development of skarn amphiboles, as here described, may be pointed out.

Radiating textures obviously require a certain freedom of growth. When a carbonate rock is replaced, growth in all directions from the centre appears to be possible, favouring the development of stellate groups approaching a spherical form. The difference in frequency of such growths, between tremolite and actinolite, is probably due to the fact that the former mostly replaces carbonate rock directly while the latter very often takes the place of an earlier formed diopside, replacing it from a fine network of veins.

In the altered siliceous rocks, on the other hand, the plane of schistosity is conspicuously preferred, as illustrated by the shape of the anthophyllite aggregates.

Most striking, and apparently inexplicable, is the textural difference between orthorhombic and monoclinic Mg-Fe amphiboles in "quartzitic" alteration products. As to the various forms of anthophyllite displayed in the Falun mine, some points of view will be presented in the following.

Examined occurrences of amphiboles

Sulfide deposits

Kaveltorp.—This lead-zinc-copper mine has been studied by Magnusson (1940). It worked a deposit of pyrometasomatic type in dolomite. The sulfides are accompanied by much skarn, highly magnesian in the lead-zinc ores and somewhat more

ferriferous with the copper and iron sulfides. The former paragenesis also shows a higher proportion of fluorine. Replacement started with the development of forsterite, followed in turn by clinohumite and chondrodite; at the same time amphiboles developed in quantity, showing an increasingly magnesian character by ranging from actinolite through tremolite to anthophyllite and cummingtonite. Fluorite and phlogopite also occur in considerable amounts.

On tremolite (grammatite) from Kaveltorp, K. Johansson (1930) has made a complete analysis, showing 0.95 per cent F.

For the present investigation a sample was prepared from a specimen, in the museum collections, of white anthophyllite in radiating groups of stalks. It has 1.15 per cent F and 0.00 Cl.

*Falun.*¹ In this deposit, by far the largest concentration of sulfides in Central Sweden, large ore bodies consisting chiefly of pyrite are, on almost their whole circumference, surrounded by a wide zone of alteration where the leptite has been changed into "quartzite", mostly with cordierite and anthophyllite, outward grading into a mica schist rich in cordierite which in turn is succeeded by unaltered leptite. In the "quartzite" there are concentrations of chalcopyrite, and some small ore bodies with considerable values in gold.

The amphibole of the "quartzite" is generally anthophyllite but gedritic varieties also occur and, as already mentioned, in rare cases cummingtonite. With the exception of the grains in the gold ores, as described above, the anthophyllite is always in the form of stellate aggregates. For analysis was chosen, for practical reasons, a sample from the outlying mineralized area at Näverberg, 4 km W. of Falun (Geijer 1917).² It has 0.24 per cent F and 0.01 per cent Cl.

The pyritic ore bodies are in part mixed with carbonate rocks, and in part quartziferous. In the former case they very often contain replacement remnants of limestone or dolomite, ranging in size up to several meters. The carbonate rock often is ophealitic, but the original Mg silicate is always altered into serpentine. The chief gangue mineral of the ore, beside remnants of carbonate, is a monoclinic calciferous amphibole, varying from almost white to green forms but always colourless in thin sections and therefore, with the usage adopted here, to be classed as tremolite. It occurs as scattered metasomes or concentrated into small skarn bodies. The relative distribution of ophealite and amphibole-bearing ore appears to indicate a less intimate connexion between the two mineralizing processes than at Kaveltorp, and sulfide deposition seems to have been hydrothermal rather than pyrometasomatic in nature.

Among amphiboles of this paragenesis there was selected for analysis a specimen from the stope "Turken", on the 312 m level in the southeastern part of the mine (Källort ore body). There, a felty mass of light grayish green tremolite with much anhydrite in grains up to 8 cm in size, and a little pyrite, forms a stripe a couple of meters in width along one side of a pyrite ore with much sphalerite and enclosing large remnants of limestone.³ This tremolite has 0.27 per cent F and 0.00 Cl.

¹ The summary here given differs in some details from the description earlier published by the writer (Geijer 1917), the difference being mainly due to continued observing of developments up to 1940.

² This area is connected with that of the Falun mine by a zone of weaker alteration.

³ This is the most conspicuous occurrence of anhydrite recorded in the Falun mine, where it is found locally in the Källort ore body. It has crystallized before the sulfides (Geijer 1917). The four other known occurrences in Central Sweden (Garpenberg, Kalvbäcken, Sala, Långban) all show paragenetical relations similar to those at Falun. The carbonate beds of the leptite formation, where not ore-bearing, are extensively quarried and thus well exposed; in them, anhydrite

Available observations on amphiboles in the sulfide bodies replacing carbonate rocks do not include any case where the supply of Mg has been sufficient to form anthophyllite instead of tremolite, as described above from Kaveltorp. However, such observations are too limited to justify any conclusion in the negative.

The quartziferous pyrite ore contains, as gangue minerals, anthophyllite and quartz. The anthophyllite forms slender stalks, rather evenly distributed in the sulfides. K. Johansson (1930) who has studied this anthophyllite, reports 0.45 per cent F. The quartz occurs as scattered grains but the ore also contains inclusions of "quartzite", in the same way as the other main type carries such of carbonate rocks. This "quartzite", however, is different from the variety that forms the altered area outside of the pyrite bodies. It is mostly glassy and contains very little silicates. The quartziferous pyrite ore, therefore, must have originated through a process somewhat different from the one that has resulted in the cordierite-anthophyllite "quartzite" and its chalcopyrite ore bodies. It is clear that the "quartzite" of the inclusions had received its characters before the pyrite invasions, while the stalks of anthophyllite are more closely related to the latter. Probably a mapping that takes into account also the various chemical and textural forms of amphiboles would shed welcome light on the processes that have been active in the forming of the Falun ore deposits.

There has also been analysed a sample of tremolite, somewhat different in its mode of occurrence from the one already described. It is from a crosscut, 20 m below datum level, in the northwestern part of the mine. There, lenses of dolomite and replacing tremolite skarn occur in a zone curving around the outskirts of the central pyritic ore body. The sample consists of stalks of a greenish white tremolite with a faint sprinkling of pyrite. This tremolite has only 0.08 per cent F.

There exists also an old analysis of tremolite from Falun, reporting 0.35 per cent F (Michaelsson 1863). The mineral is described as pale green, half translucent prisms in "talc schist". The exact locality is not given, but the description indicates that the occurrence may be similar to the one just described.

Iron ores, Källfall type

Two samples have been analysed, both from the Riddarhyttan district (compare above). One specimen from the Källfall mine has anthophyllite in stellate groups, in magnetite ore; this anthophyllite has 0.41 per cent F. Another specimen, from Persgruvan, is a lean ore with much anthophyllite in similar "stars", and cordierite, both chiefly in a band 2.5 cm wide. In this case the anthophyllite contains 0.66 per cent F.

Iron ores, pyrometasomatic type

Sjögruvan in Svärdsjö (Geijer 1939) is an example of the magnetite paragenesis with ludwigite, in dolomitic limestone. Other associated minerals are serpentine with small remnants of an orthorhombic mineral (forsterite or humite), and brucite. More subordinate skarn forms are such of forsterite and tremolite, and of diopside,

has never been observed. It therefore appears impossible to apply to the occurrences in Central Sweden the interpretation currently given of the paragenetically similar occurrences in the Grenville of eastern North America (as in the Edwards-Balmat sulfide district) which are regarded as metamorphic deposits of sedimentary origin.

both kinds also with magnetite, while garnet is found only as lumps enclosed in the diopside skarn.

The analysed material is from a very fine-grained, greenish white tremolite skarn; it has 0.23 per cent F.

Norra Skilå mines, Riddarhyttan (Geijer 1923). Magnetite ore and skarn consisting of tremolite and low-iron diopside replace ophicalcite. The light yellowish tremolite has 0.42 per cent F and 0.014 per cent Cl.

Östanmossa in Norberg (Geijer 1926, 1936). Skarn ore deposit replacing limestone and dolomite (in part ophicalcitic). The most common type of skarn is actinolite with remnants of diopside, generally of microscopic size only. Skarn of an andradite garnet is more subordinate. Tremolite skarn occurs in considerable quantity and apparently replaces carbonate rock directly; with it are, beside magnetite, humite minerals, phlogopite, and locally various cerium minerals. From a sample of the typical actinolite skarn, material for analysis was separated, but the small inclusions of diopside could not be satisfactorily eliminated. The amount of such, however, was estimated to be less than ten per cent. The figure obtained for the actinolite, 0.51 per cent F, thus is slightly too low. Tremolite for analysis was taken from a specimen containing also much magnesium orthite, from the drift on the 47 m level that is the type locality for the orthite variety in question, as well as for norbergite (Geijer l.c.). There, tremolite and magnesium orthite replace the dolomite alongside a small ore body of magnetite and tremolite; norbergite occurs in the same area but is not so regularly associated with the other replacement products. The tremolite of the sample is fine-grained, greenish white, similar to the analysed specimen from Sjögruvan. With it are much orthite and a little magnetite. F in the tremolite is 2.34 per cent and Cl 0.01 per cent.

Åsgruvan in Norberg (Geijer 1936, Sarap 1957), distant only about 400 m from Östanmossa, is rather similar to the latter in its geological characters. The skarn is chiefly diopside, rather low in iron and more or less replaced by actinolite. Tremolite and humite minerals occur very much as at Östanmossa, but norbergite has not been identified and cerium compounds are more rare. Andradite garnet also occurs, and in two forms: one is similar to the garnet skarn of Östanmossa; the other has been the last skarn mineral to form, developing as thick veins of large and beautifully zonal garnet crystals with some sulfides, quartz, and scheelite. A very careful optical study of skarn minerals from Åsgruvan has been carried out by Sarap (1957), showing, among other details, a wide range of chemical variation within the tremolite-actinolite series. Unfortunately, the geological and paragenetical relations of the various specimens are not reported.

As at Östanmossa, two samples of amphiboles have been selected for analysis. One represents the ordinary actinolite skarn; in this case the grayish green, very fine amphibole felt was found to be free from diopside. F is 0.78 per cent. The other sample is of a greenish white tremolite associated with chondrodite and a little magnetite, pyrite, and chalcopyrite, the whole replacing dolomite. In this case F in the amphibole is 1.03 per cent.

Iron ores, reaction skarn type, non-manganiferous

Örling mine (Morberg field), Norberg (Geijer 1936), has been chosen as a typical representative of the sedimentary quartz-banded iron ores. The ore mineral is chiefly hematite. Magnetite occurs more subordinately; as is always the case in this ore type

it is a product of metamorphism of hematite ore. Skarn minerals occur frequently but not in any greater quantity. Andradite garnet forms narrow reaction zones between bands of hematite and such of quartz, but also occurs as large, lens-shaped concretions, roughly parallel to the bedding. Actinolite is not quite as common. It occurs as thin bands alternating with those of ore (then always magnetite), and thus takes the place of the quartz bands.

The specimen chosen for analysis consists of finely quartz-banded magnetite ore in which some bands are actinolite instead of quartz. The actinolite is light green, approaching tremolite. It has 0.40 per cent F.

Konstgruvan in Norberg. This is in the area referred to above as an instructive case of reaction skarn. Numerous outcrops show a green actinolite skarn with lumps of andradite, stripes of magnetite and of vein quartz. Sometimes also lumps of unaltered quartz-banded ore, some decimeters in length, are enclosed. For analysis was chosen a piece of actinolite skarn from the dumps at the abandoned small mine Konstgruvan. This actinolite contains 0.72 per cent F and 0.00 Cl.

Kallmorberg in Norberg (Geijer 1936, Magnusson 1953). This mine works one of the most interesting iron ore deposits of the region and therefore requires as detailed a description as space may permit. There are several parallel bodies of ore. The main type is a magnetite ore with skarn, but there is also found magnetite in carbonate rocks (varying from limestone to dolomite) and beds of quartz-banded hematite.

The "limestone ore" in the western part of the mine is accompanied by some skarn (tremolite to actinolite) and partly shows typical replacement relations to the surrounding dolomite which is ophicalcitic in the neighbourhood of the ore. Also norbergite and chondrodite occur in this association, but only in small quantities. While these features suggest an origin through pyrometasomatism, the ore appears to grade eastwards into a form in which magnetite and actinolite together occur as bed-like bands in the carbonate rock. Further eastwards, again, the limestone contains regular intercalations of magnetite ore, with or without quartz-banding. Also beds of finely quartz-banded hematite ore occur.

The skarn ore bodies of the middle and eastern parts of the mine contain magnetite in a very uneven distribution, varying from concentrations of rich ore to skarn almost free from magnetite. The characteristic skarn mineral is a deep green actinolite, but occasionally patches of andradite are noted. Here, too, there have been observed remnants of quartz-banded ore enclosed in the massive skarn ore.

The picture is further complicated by the fact that the leptite surrounding the deposit is in places, and seemingly rather erratically, altered into a "quartzite" with much almandite, gedrite, or andalusite, sometimes also tourmaline. This alteration often reaches the contact with carbonate rock, without producing any appreciable changes in it. Copper ore, chiefly chalcopyrite, accompanied by much fluorite, is found at several places and has even formed an ore body of several thousand tons. Its development appears to be later than that of the skarn ore. General experience from the region makes it pertinent to suspect a close relation between this sulfide mineralization and the rock alteration just mentioned.

The evidence that can be obtained from this complicated deposit will be discussed in the following.

The actinolite for analysis was separated from an ore specimen from the Norr-Mellangruvan ore body on the 182 m level, in which it occurs as stripes in fine-grained magnetite. It has 0.40 per cent F.

Långgruvan in Norberg (Geijer 1936). This deposit is situated 3 km N.E. of Kallmor-

berg and is similar to the latter in many features. However, no carbonate rocks are present. There is a highly deformed bed of skarn ore with such an even distribution of the magnetite that practically the whole bed has been mined as a concentrating ore. Magnetite and skarn alternate in a way that suggests a disturbed bedding. The skarn is a rather dark green actinolite. In portions of the ore bodies, especially where indications of strong pressure can be noted, anthophyllite and biotite appear instead. Irregular stripes of quartz are frequent, and reach a greater thickness than normally encountered in the quartz-banded ores of the region. Fluorite is often present in the quartz bands, and also occurs as stripes in the skarn. A little chalcopyrite is associated with it. In one place a small concentration of copper ore with fluorite was found, enclosing lumps of magnetite ore with actinolite. Alteration of the wall rock into "quartzitic" forms is only local at Långgruvan.

A sample of the typical skarn actinolite was found to contain 1.17 per cent F. This unexpectedly high figure raised suspicion that a few grains of fluorite might have escaped notice and become included. A new separation was therefore made from the same specimen and subjected to special control; it gave 1.16 per cent F and 0.00 Cl. A sample of the anthophyllite, on the other hand, showed only 0.31 per cent F.

For the interpretation of the geological history of this deposit it is necessary to consider also the small mine Skansgruvan, about 200 m W. of Långgruvan. It has a quartziferous magnetite ore, most of it regularly banded but in part with bands of fluorite instead, even up to more than half the volume of the ore. There is also a bed of andradite-fluorite skarn, with some chalcopyrite.¹ The leptite wall rock immediately adjacent to the ore is altered into a "quartzite" rich in almandite and with megascopically visible tourmaline.

Rudgruvan, Fagersta (Geijer, in Geijer and Magnusson 1944), about 15 km S.W. of Kallmorberg, belongs to the same general type of skarn ore as the latter and Långgruvan. It forms the northeasternmost part of a bed of skarn ore that is, apart from possible small dislocations, continuous for 2.4 km. The ore is rather similar to that of Långgruvan. Thus the skarn is a dark green actinolite, or darker hornblende; pyroxene, andradite, and epidote are rare. Stratification of ore and skarn is more regular and in part finer than at Långgruvan. Some beds of skarn without magnetite alternate with the ore. Zones of pressure are marked by biotite and almandite appearing instead of amphibole. At other points in this long ore zone, bands of quartz, and even of quartz-banded ore, have been noted. Of fluorite, so conspicuous at Långgruvan, there has been observed only a single stripe.

The sample selected for analysis consists of magnetite and a dark green hornblende, with the absorption colours of "common hornblende". This hornblende carries 0.19 per cent F and 0.20 per cent Cl.

Hällsjö mine in Vika (Geijer in Geijer and Magnusson 1944) is a small mine, not worked since the turn of the century. The dumps show the deposit to be essentially like that of Rudgruvan (distance about 45 km). Its ore is magnetite with a greenish black hornblende, alternating as fairly regular seams or more streakily. Andradite skarn is quite subordinate. Patches of vein quartz with hornblende, epidote, and sometimes scheelite, probably are due to the influence of the neighbouring granite (Earlier Svionian group). Hornblende was separated from a specimen in which it forms seams up to 1 cm thick, with a distinct schistosity by crystallization. It has 0.68 per cent F and 0.017 per cent Cl.

¹ This is the same paragenesis as in the Stripåsen copper mine, 500 m to the S. (Geijer 1936, 1958).

Persberg (Magnusson 1925). In this important skarn ore district the most common form of ore deposits is one in which magnetite occurs rather irregularly in a skarn made up of andradite garnet and pyroxene (hedenbergitic diopside), the latter partly replaced by amphibole. More locally the Ca-Fe skarn has been replaced by a pronouncedly magnesian one, with anthophyllite as the predominant skarn mineral. There occur also, in the associated carbonate rocks, ores with forsterite and serpentine, etc. These relations are interpreted in the following way (Magnusson l.c.). The garnet-pyroxene skarn is a product of interior reactions in a siliceous iron deposit formed during the building up of the leptite formation, the reactions having been started by regional heating in connexion with folding and the intrusion of the Earlier group of Svionian granites. The magnesian forms, again, are the results of the action, later in the same orogenic epoch, of the magnesia metasomatism on these earlier skarns, the replacing of the iron in them by magnesium setting free iron and thus increasing the proportion of magnetite.

The different kinds of amphiboles occur in the following ways. Actinolite is common in the pyroxene skarn as a later replacement but does not form separate bodies. Its place is to some extent, chiefly near the leptite wall rock, taken by hornblende. Tremolite is rarer than actinolite but is the main constituent of some skarn bodies of moderate size, together with mica (presumably phlogopite) and olivine. The mode of occurrence of the anthophyllite has already been reported. It is characteristic of the Alabama ore body but has largely become altered to talc. Cummingtonite is rare.

Magnusson (l.c.) gives a number of analyses of skarn varieties. As the skarns as such have been analysed, not the separate minerals, the figures are not directly comparable to those from the actual investigation. An analysis of tremolite skarn shows 0.40 per cent F, but Magnusson remarks that the high fluorine is due to the presence of mica. More unexpected is the figure for anthophyllite, calculated from an analysis of ore consisting only of magnetite and such amphibole; it gives only 0.05 per cent F which, with the high H_2O (4.11), gives a fair correspondance to the anthophyllite formula. This is the more remarkable as the anthophyllite here often is paragenetically associated with much fluorite. It might suggest that fluorine has in the first place combined with the available calcium, only the excess entering into the amphibole. But an analysis of a talc sköl in which the talc is, at least in part, pseudomorphous after anthophyllite, shows 0.47 per cent F. It is then not possible to form any opinion on the role of fluorine in the Persberg anthophyllite. Unfortunately no material for a new analysis has been available.

Taberg in Värmland (Magnusson 1929). This deposit, situated 13 km N.W. of Persberg, exhibits similar relations between an earlier skarn generation of garnet and pyroxene and a later one of more magnesian skarn, in this case mainly tremolite and low-iron diopside. Little magnetite occurs disseminated in the skarn, the ore bodies forming irregular concentrations generally next surrounded by the lighter-coloured skarn type. No good sample of the tremolite has been available, and for analysis was chosen a specimen of green actinolite skarn; the amphibole forms short stalks in a crystalloblastic texture. The percentage of F is 0.40.

Nordmark mine (Magnusson 1929). No skarn amphibole from this deposit, essentially like that of Taberg near by, has been analysed. But there has been published an analysis of a tremolite from Nordmark that in its paragenetical relations comes very close to the skarn; for this tremolite 0.00 per cent F is reported (quoted in Du Rietz 1935). This tremolite occurs in fissure fillings in the magnetite ore, as prisms growing out from the walls; crystals of magnetite also occur, and the rest is filled

by calcite. The occurrence has been described by Flink (1888), and the material used for analysis was from a specimen collected by him. Considering the fact that no skarn-forming tremolite in the region has been found free from fluorine, the reported absence of this element suggested the possibility that tremolites belonging to a presumably slightly later phase of mineralization might differ from the skarn-forming ones in this respect. Therefore a new analysis was made, on a specimen of the same nature, in the material collected by Flink and belonging to the museum. This analysis gave 0.34 per cent F.

Iron ores, reaction skarn type, manganiferous

Basttjärn in Ljusnarsberg (Magnusson 1940) is a typical example of this group of deposits when occurring as regular beds. The ore consists of magnetite more or less mixed with skarn silicates. Of the latter, knebelite is most common, with dannemorite (manganiferous grunerite) next. The dannemorite has formed after the knebelite. There is, on the whole, an uneven distribution of these silicates, with the knebelite predominating in the central parts of the ore bodies and the dannemorite mainly in the peripheral portions. Towards the leptite walls of the deposit there further appear garnet, biotite, pyroxene, and hornblende, and these minerals may gather into more or less continuous boundary skarn bodies, penetrating also some distance into the leptite. As the chief component of the latter is microcline, a source for the Al and K contained in this skarn is indicated. Small amounts of sulfides (pyrite, chalcopyrite, and pyrrhotite) are found in this skarn, and a little fluorite.

Magnusson (l.c.) has published four analyses of skarn minerals from Basttjärn, including both kinds of amphiboles. These latter are of so much interest that they are here reproduced in full (Table 1).

The very high chlorine in the hornblende is especially noteworthy and contrasts with its absence in the dannemorite.

Klackberg in Norberg (Geijer 1936). In this deposit silica reaches only about 3 per cent. A considerable amount of the original Mn-Fe carbonate still exists with the magnetite. Towards the surrounding dolomite the ore bodies show replacement contacts. Because of the low silica, skarn minerals are very subordinate. It is remarkable that knebelite has not been identified, dannemorite being the only silicate found within the ore bodies. No concentrations of skarn occur in the ore, but reaction zones have formed where ore comes into contact with the leptite that surrounds the dolomite body and also occurs interstratified with it as a number of thin beds. Such reaction zones are narrow, mostly not more than a few decimeters in width. Their minerals are spessartitic garnet, dannemorite, and black mica, in varying proportions. As a rule there is a straight boundary against the ore, evidently marking the original limit of the leptite; inwards in the leptite the skarn ends with an irregular contact and often a zone of scattered skarn silicates beyond it. It is clear that the carbonatic ore, mixed with some dolomite, has supplied the Mn, Fe, and Mg, while of the components of the leptite Al and Si have largely remained, and to some extent also K.

The sample used for analysis is from the Storgruvan ore body on the 285 m level of the mine and represents the replacement of a narrow bed of leptite at its contact with ore containing some dolomite. It consists of small garnets and a fine felt of amphibole needles, grayish yellow in colour. The refraction of the amphibole is $\gamma = 1.685$ which according to Sundius (1931) indicates about 40 per cent of the Fe-Mn silicate. It has 0.20 per cent F and 0.037 per cent Cl.

Table 1. Analyses of amphiboles from Basttjärn (from Magnusson 1940).

	Dannemorite	Hornblende
SiO ₂	48.72	36.22
TiO ₂	0.00	0.00
Al ₂ O ₃	0.22	10.54
Fe ₂ O ₃	1.15	6.70
FeO	37.99	26.42
MnO	5.35	2.45
MgO	3.40	1.29
CaO	1.04	9.72
Na ₂ O	0.17	0.61
K ₂ O	0.02	3.14
H ₂ O < 105°	0.00	0.04
H ₂ O > 105°	1.59	0.90
F	0.14	0.11
Cl	0.00	1.42
CO ₂	0.00	0.69
	99.79	100.25
Less 0 for F and Cl	0.06	0.37
	99.73	99.88

In the dolomite outside the ore bodies there occurs in small quantities a non-manganiferous skarn of amphibole, diopside, and andradite. It has probably been formed through reactions involving the dolomite and a small amount of quartz in it.

Väster-Silvberg in Norrbärke (Hjelmqvist in Geijer and Magnusson 1944) is a zone of ore deposits, about 4 km long, in which magnetite and sulfides (mainly galena and sphalerite) occur in a highly manganiferous limestone. There is much skarn, partly manganiferous and made up of knebelite, dannemorite, manganhedenbergite, rhodone, pyroxmangite (sobralite), and manganese garnet. Other skarn masses are built up of non-manganiferous silicates. Fluorite is common, especially with the sulfides. The leptite wall rock is altered into one consisting of quartz, almandite, anthophyllite, cordierite, and biotite.

The great amount of fluorite made it desirable to include a sample from Väster-Silvberg in the investigation, although it is doubtful whether this mineral was introduced in any connexion with the development of the skarn. The sample, collected by Sundius, is from Stollberg, the southern end of the ore zone, and probably taken from the dumps. It consists of a yellowish green amphibole, knebelite, galena, and magnetite. The amphibole has $\gamma = 1.710$, indicating about 80 per cent of the Fe-Mn silicate. Its content of F is 0.28 per cent.

Tunaberg (Palmgren 1917, Magnusson in Geijer and Magnusson 1944). In the gneiss territory of Södermanland the manganiferous skarn ores are sometimes developed in the metamorphic form called eulysite (Erdmann 1849), a rock made up chiefly of pyroxene, garnet, and knebelite, with but little magnetite. The largest and best known occurrence is that of Stora Uttersvik in Tunaberg. The thick bed of eulysite towards its boundaries changes into an aggregate of dannemorite and manganiferous almandite. More subordinate, in the very border zone, are hornblende, biotite, feldspar, and quartz. A peculiar geochemical feature of the eulysite is its high phosphorus

figure, 0.20 per cent, which is 20 to 50 times the amount normally found in this ore type. The eulysite is cut by a number of large pegmatite dikes.

A dannemorite from this locality has been analysed by K. Johansson (1930) who reports 0.07 per cent F.

Discussion

To facilitate comparison the analytical data are here repeated in tabular form (Table 2). Although these analyses represent only a sparse net of observations, and conclusions are also hampered by the general scarcity of figures for comparison, certain features of geochemical and geological interest are indicated.

To consider first the *fluorine*. The figures for the amphiboles from Kaveltorp,

Table 2. (See text.)

	Per cent	
	F	Cl
<i>Sulfide deposits</i>		
Tremolite, Kaveltorp	0.95	
Anthophyllite, Kaveltorp	1.15	0.00
Anthophyllite, Näverberg near Falun	0.24	0.01
Anthophyllite in pyrite ore, Falun	0.45	
Tremolite (with anhydrite), Falun	0.27	0.00
Tremolite, Falun	0.08	
Tremolite, Falun	0.35	
<i>Iron ores, Källfall type</i>		
Anthophyllite, Källfall mine	0.41	
Anthophyllite, Persgruvan	0.66	
<i>Iron ores, pyrometasomatic type</i>		
Tremolite, Sjögruvan (Svärdsjö)	0.23	
Tremolite, Norra Skilå mines	0.42	0.014
Tremolite, Östanmossa	2.34	0.01
Tremolite, Åsgruvan	1.03	
Actinolite, repl. diopside, Östanmossa	0.51	
Actinolite, repl. diopside, Åsgruvan	0.78	
<i>Iron ores, reaction skarn type, non-manganiferous</i>		
Actinolite, Örling mine	0.40	
Actinolite, Konstgruvan (Norberg)	0.72	0.00
Actinolite, Kallmorberg	0.40	
Actinolite, Långgruvan (Norberg)	1.17	0.00
Anthophyllite, Långgruvan (Norberg)	0.31	
Hornblende, Rudgruvan	0.19	0.20
Hornblende, Hällsjö mine	0.68	0.017
Actinolite, Taberg	0.40	
<i>Iron ores, reaction skarn type, manganiferous</i>		
Dannemorite, Basttjärn	0.14	0.00
Hornblende, Basttjärn	0.11	1.42
Dannemorite, Klackberg	0.20	0.037
Dannemorite, Väster-Silvberg	0.28	
Dannemorite, Tunaberg	0.07	

chosen as an example of a typical pyrometasomatic sulfide deposit, are quite ordinary from a mineralogical point of view, yet call for a revision of the view generally held about the quantitative role of fluorine in such deposits of this metallogenetic province. For it has hitherto, expressly or tacitly, been assumed that this role could be judged almost entirely from the abundance of such minerals as fluorite, humites, and phlogopite. The proportion between these minerals and amphiboles, in the Kaveltorp deposit, cannot be exactly stated, but it appears clear that the much larger amounts of amphibole skarn must represent a quantity of fluorine quite comparable to that contained in the minerals higher in this halogen.

The amphiboles of the Falun mine show a lower range. This may be due either to a regional variation or to a somewhat different mode of origin, including probably a slightly lower temperature of formation. The extremely low figure, 0.08 per cent F, in one tremolite is unexpected, however.

Anthophyllites from iron ores of the Källfall type illustrate local variations and show higher figures than the anthophyllite of the "quartzite" at Närke near Falun, of comparable mode of origin.

Of the other types of iron ore, the pyrometasomatic one presents, as might have been expected, figures comparable to those of the paragenetically comparable sulfide deposit of Kaveltorp. The tremolites that directly replace carbonate rock show a wide range, however, from 0.23 to 2.34 per cent F. It was expected that the tremolite from Östanmossa would show such an unusually high figure, as it was chosen for analysis in order to illustrate the percentage of fluorine in an amphibole associated with other silicates remarkably high in this component: norbergite with 13.60 per cent F, and magnesium orthite with 3.11 per cent, a unique figure for a mineral of the epidote group. Apparently there are here indicated conditions of formation that implied unusual proportions in the mineralizing emanations. It is also of interest in this connexion to note that the tremolite from Åsgruvan, associated with chondrodite, has 1.03 per cent F, and that the lowest value, only 0.23 per cent, is found at Sjögruvan where no humite mineral has been identified but forsterite skarn occurs.

As to the actinolites in this group (from Östanmossa and Åsgruvan), their percentages of fluorine are somewhat lower than those in tremolite from the same deposit. This fact, however, hardly indicates any appreciable difference in the nature of the mineralizing agents, but may be wholly due to a different kind of emplacement: while the analysed tremolites directly replace carbonate rock, the actinolites have originated through the replacement of earlier formed diopside and consequently with less quantitative change.

It is in the great group of non-manganiferous iron ores with "reaction skarn" that this investigation has given unforeseen results. It has been held, on strong field evidence, that these skarns have formed as a result of regional heating, through reactions between the components originally present in the deposit. Truly, the frequently irregular distribution of the new-formed minerals indicates that a transporting agent has been active in this process but does not appear to require the presence of any greater amount of water than is currently supposed to be of normal occurrence in the rocks. It has even been maintained that these reactions could have taken place entirely without the intervention of such a factor. Thus Magnusson (1954) expresses the belief that these skarns "must have been formed through reactions in the solid state. Small amounts of water have naturally been present here and there." Later experimental work (Hedvall 1958), however, has shown that the minerals then sought for, andradite and diopside, could not be produced through reactions in the solid state

within such conditions of temperature and pressure that are to be reckoned with in this case. On the other hand, both minerals were obtained in the presence of water vapour.

The following considerations apply only to the amphiboles and cannot be indiscriminately extended to such skarn minerals as garnet and diopside.

The amphiboles of the skarn iron ores in question have been found to carry fluorine generally within the same percentage range as those of pyrometasomatic origin, apart from the exceptional Östanmossa tremolite among the latter. The sample from Taberg, the only one that had earlier been interpreted as a product of magnesia metasomatism alteration of an earlier, reaction skarn, is not among those higher in fluorine. If the rest, all regarded as reaction skarns proper, had been formed in the way hitherto assumed for such, this would require an original amount of fluorine quite at variance with what is known or surmised about the original nature of these deposits. Concentration from the surrounding rocks—"lateral secretion" in a wide sense, or metamorphic differentiation—may possibly explain a local supply of fluorine higher than the normal but obviously fails as an explanation when fluorine percentages of 0.40 and more are present in continuous skarn bodies ranging into thousands and hundreds of thousands of tons. Whatever the ultimate source of the fluorine, the containing formation is inadequate as such, and this source must be sought outside it.

The conclusion then seems inevitable that these fluorine-bearing amphiboles, like those of the pyrometasomatic deposits, have formed during the period of the magnesia metasomatism—comprehending then, as usual, under this term all the metasomatic activities, varying somewhat, with the time and the place, in their chemical and physical aspects, that were due to the introduction of emanations into the leptite formation in connexion with the intrusion of the Earlier Svionian granite group. For this geological dating there is very strong evidence, some of which will appear from the above descriptions. Also a correlation with earlier or later geological events is excluded, the alternative earlier because there is no trace of any earlier chemical attack on the leptite formation, much less so of one felt all over the region, and the alternative later by the fact that all later metamorphic processes have had entirely different results, as illustrated particularly well through Magnusson's studies in the Filipstad district (Magnusson 1925, 1929).

Facts are also known that permit further conclusions with regard to the role of the magnesia metasomatism in the development of the amphibole skarns hitherto regarded as products of interior reactions. The Kallmorberg deposit is particularly instructive. As will be seen from the above description, its least siliceous part, the "limestone ore", exhibits features that correspond to what might be expected if agents of the magnesia metasomatism were brought into contact with a pre-existing bedded ore in carbonate rock, with resultant local transport of iron and loss of the regular bedding. More important still are the characters of the main ore type of the mine, that with abundant actinolite skarn. It will be remembered that this variety contains remnants of quartz-banded ore and therefore, at least the bulk of it, is interpreted as a "re-arranged" deposit which, those local remnants excepted, shows almost no traces of the original distribution of iron and silica, and of their relations to the associated dolomite or limestone. Now the considerable amount of fluorine (0.40 per cent) in a typical sample of the actinolite indicates that this skarn is essentially a product of the magnesia metasomatism. There are strong reasons for believing that it represents the direct result of the action of the agents of this metasomatism on the quartz-banded ore beds in the carbonate rocks, and that, consequently, the

deposit has never passed through a stage when it was developed as a reaction skarn in the proper meaning of this term. For one frequently finds at Kallmorberg that quartz-banded ore is in contact with carbonate rock without even the slightest development of skarn at the boundary surface. Therefore regional heating by diffusion, the factor to which the forming of reaction skarns has been ascribed, cannot have caused the great transformations in the ore bodies with actinolite skarn, often only some few meters distant from the contacts undisturbed by reactions. It seems clear that not only some substances contained in these ore bodies, as the fluorine, were contributed by the emanations of the magnesia metasomatism, but that these emanations furnished also the heat necessary for the reaction, presumably also a quantity of water considerably above that normally contained in the rocks. It is possible, and in the opinion of the writer even probable, that also some iron was contributed in this way, but this possibility does not affect the conclusion that "re-arrangement" of a sedimentary deposit was here the main factor in giving the deposit its present aspect.

The possibility that reaction skarn formation and magnesia metasomatism may sometimes have coalesced into one process has, on general grounds, been pointed out earlier (Magnusson 1940). As to the transfer of heat by solutions, in ordinary contact metamorphism, reference is made to a study by Gilluly (1932).

An interpretation similar to the one here given for the Kallmorberg deposit is probably applicable to many other occurrences of amphibole skarns. On the other hand, there are many cases known where such skarn was preceded by one consisting mainly of pyroxene. And it is, as already emphasized, not justifiable to extend the conclusions founded upon the characters of the amphibole skarns to such made up typically of pyroxene and garnet. But the fact that, like these, amphibole skarns may occur as thin seams interbedded with leptyte, suggests that the agents that caused the forming of amphiboles may have penetrated the leptytes without producing in them any of the alterations that constitute, in other cases, the most spectacular results of the magnesia metasomatism.

The amphiboles of the manganiferous ores form a group apart, their content of fluorine being on the average markedly lower than in any other group. It is therefore impossible to say whether the above conclusions concerning the origin of the amphiboles in the non-manganiferous reaction skarns can be applied also to this group. It is worthy of note, however, that the highest figure (0.28 per cent) is found in the Väster-Silvberg deposit where the magnesia metasomatism has wrought great changes in the country rock and also in the deposit itself, including the introduction of much fluorine that was fixed as fluorite. Also the value from Klackberg, 0.20 per cent, seems remarkably high if interpreted as the result of concentration from a limited neighbourhood, as implied by the original meaning of the term reaction skarn. Other values are lower, and as the amphibole is only one of several important skarn constituents, the total amount of fluorine indicated for these deposit may possibly be explained without reckoning with contributions from the outside.

Anyway it is clear from the data here presented that fluorine was contributed during the magnesia metasomatism in considerably greater quantities than has previously been assumed. Unknown still are the amounts contained in those quantitatively predominant products of this metasomatic action, the mica schists. The most widespread variety, a quartz-rich muscovite-biotite schist with much cordierite, contains no amphibole and, beside the micas, no other fluorine-bearing mineral apart from the sporadic tourmaline. In order to get quantitative data on the content of fluorine in these schists, one should have to make a great number of analyses, troublesome be-

cause of the difficulty of preparing average samples from rocks in which the cordierite ellipsoids frequently reach decimeters in size. To get at least a qualitative idea, three specimens have now been analysed. One, from Riddarhyttan, is of a specimen already analysed, but then without determination of the fluorine (compare Geijer 1923, p. 23, analysis no. IV). It is a schist without cordierite, with much mica, both muscovite and biotite; it has K_2O 4.34 per cent, and MgO 3.09. The F percentage is 0.16. Another sample is a rather fine-grained schist from the Lerklockan mine in the same district, it has only 0.07 per cent F. At the Skyttgruvan mine, in the immediate neighbourhood of Näverberg (compare above), there is a schist containing ellipsoids of cordierite up to about 2 dm in size, enclosing grains of quartz and a little biotite, in a groundmass of muscovite, biotite, and quartz. A sample in which the cordierite may have been underrepresented, showed 0.21 per cent F.

In the original rocks, before alteration set in, the only possibly fluorine-bearing minerals were micas. Their quantity is always much too small, however, for them to have furnished the amount of fluorine present after alteration. The fluorine percentages here reported thus indicate that this element has been introduced, at the alteration into mica schists, in amounts quite comparable to those in products of the common type of hydrothermal sericitic alteration (compare Paige and Steiger 1918, Ödman 1942). The average content may seem low compared to that of the amphibole skarns, but instead the quantity of altered rocks is very much greater.

There are two more aspects of the geochemistry of fluorine in the magnesia metasomatism that deserve mention: the absence of topaz, and the mode of occurrence of fluorite.

Since many minerals containing fluorine occur in the parageneses of the magnesia metasomatism, the writer long ago made a special search for topaz among the aluminium-rich alteration products, such as the andalusite "quartzites". But it has never been found in them, nor have any probable pseudomorphs. It appears therefore that the physico-chemical conditions for its formation have not been realized, whether this depends upon a too low temperature or on other factors.

The distribution of fluorite is very uneven. In the sulfide deposits formed by pyro-metasomatic replacement of carbonate rocks it is present in great quantity in a few, but mostly scarce or lacking, and in the paragenetically comparable iron ore deposits it seems to be entirely absent. As might be expected it appears to have formed mainly when the replaced rock was a pure limestone, and the proportion Fe:Mg in the introduced substances was high.

As to the altered siliceous rocks, they were originally poor in calcium, and the alteration has further reduced the content; in three analyses of mica schists from Riddarhyttan the maximum percentage for CaO is 0.12 (Geijer 1923). Occurrence of much fluorite in such rocks obviously means that not only fluorine but also a corresponding amount of calcium has been introduced. Fluorite occurs with quartz in quantity in some iron ores where the wall rock is altered into a "quartzite" with silicates of Mg, Fe, and Al, as exemplified by the Skansberg mine described above. But in the mica schists and the "quartzites" themselves it is extremely rare. A most notable exception from this rule is met with in the sulfide deposits of Garpenberg. Both proportions of ore minerals (sphalerite, galena, chalcopyrite, pyrite) and of associated minerals vary greatly within this limited field. Fluorite is restricted to a belt of light-coloured mica schist where, together with chalcopyrite and quartz, it

forms stripes following the steeply dipping schistosity and filling horizontal joints; the quantity of fluorite is considerable.¹

This paragenesis thus seems to be later than the alteration into mica schist, but is restricted to the same belt. In cases of this nature, a hydrothermal solution is indicated as the probable transporting agent.

As could be expected for several reasons, *chlorine* shows a distribution quite different from that of fluorine. In the amphiboles with only bivalent cations the highest value recorded is only 0.037 per cent. Of the three hornblendes, a "common" one has 0.68 per cent F and only 0.017 Cl while the other shows respectively 0.19 and 0.20 per cent; finally the hastingsitic variety from Basttjärn has 0.14 F and 1.42 Cl.

It is not quite certain that the remarkably chlorine-rich ferrohastingsite is a product of the same geochemical process as all the other examined amphiboles. For the Later Svonian granites which are known to have been in several places accompanied by the formation of scapolite, occur also in the neighbourhood of Basttjärn. And at Tennberg, about 6 km E of Basttjärn, a granite body of this group encloses blocks of limestone and has produced intense contact metamorphism, including the formation of scapolite in the contact granite (von Eckermann 1923). Since the ferrohastingsite of Basttjärn clearly belongs to a later phase of skarn formation than the bulk of typical manganiferous skarn in the deposit, a genetical connexion with the later granite group is not excluded. But, on the other hand, Magnusson's (1940) description of its paragenesis gives a picture fully consistent with the interpretation that this later skarn is a product of the agents of the magnesia metasomatism acting upon the reaction skarn of the deposit and on its wall rock.

Data for comparison with the chlorine percentages listed here are extremely few. Of chlorine determinations in amphiboles with only bivalent cations, the highest value known to the writer is 0.05 per cent, in an anthophyllite (Kuroda and Sandell 1952). All higher values previously reported are in hornblendes, and particularly in hastingsites (Buddington 1952, Buddington and Leonard 1953). The data presented here thus give the same picture as the earlier ones. Any considerable amounts of chlorine have so far never been recorded in amphiboles with only bivalent cations, occasionally in hornblendes, and among them regularly in the hastingsitic ones. The high chlorine values in the latter are the more noteworthy as the analysed specimens represent widely different modes of origin.

It is clearly not permissible to draw, from the virtual absence of chlorine in an amphibole skarn, the conclusion that this element was not among those present at its formation. Such a conclusion would be justified only if it could be assumed that chlorine could compete, as it were, on equal terms with fluorine for a place in the amphibole structure. And this is almost certainly not the case.

An illustrative occurrence may be presented. The many and in part very large pyrometamorphic iron ore deposits of northernmost Sweden contain a skarn of diopside, tremolite, chondrodite, and phlogopite, thus with a good deal of fluorine. That chlorine also was present is shown by the frequent occurrence of scapolite, sometimes within the deposit itself but chiefly in its feldspar-bearing wall rock (Geijer 1918, 1929, 1931). This is also the case at Magnetgruvan, an old mine opening in the large Junosuando ore field at Masugnsbyn (Geijer 1929). From a sample of ore at this locality, a rather coarsely prismatic, light green tremolite was isolated for analysis. It proved to have 0.65 per cent F and only 0.01 per cent Cl.

¹ Scheele's classical studies on hydrofluoric acid were made on fluorite from this locality (and Gladsax).

Therefore, while the quantity of chlorine contained in the skarn amphiboles of Central Sweden seems to be very small compared with that of fluorine, this fact does not permit any conclusion about the proportion of these two halogens in the emanations that formed the agents of the magnesia metasomatism. An assumption that chlorine was more subordinate in them must rest entirely upon the absence of scapolite in these parageneses, a feature that is suggestive but by no means conclusive evidence.

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On structure determinations from Patterson maps

By INGVAR LINDQVIST

A great number of crystallographers have determined crystal structures using Patterson methods. The only comprehensive, systematical treatment has, however, been given by Buerger in his papers and in his excellent book, *Vector Space* (Wiley, New York 1959). He has shown that the Harker-implication method will lead to solutions in all cases with higher symmetry than triclinic, if the Patterson map can be treated as a vector set of discrete points. The image-seeking with minimum functions is an improvement suggested by Buerger for more complicated cases. Finally he has introduced the minimum function as an aid also for the search of single inversion peaks from Harker functions with large overlap (*Vector Space* p. 296). The latter method can easily be developed for other space-groups and it is of large value in cases which are "near the limit of complexity where a solution of the structure is possible", because a single peak cannot easily be recognized (*Vector Space* p. 273).

In the following a method to use the *unsymmetrical* rather than the symmetrical vectors will be developed for three different space-groups. The disadvantage of the symmetrical vectors is that with increasing complexity the interpretation of the Harker regions of the Patterson function will be seriously affected by increased overlap and particularly by the presence of non-Harker peaks. The method also gives a useful systematization of the Patterson peaks and will rapidly reveal any large error in the Fourier calculations.

Space-group $P\bar{1}$

The symmetry $\bar{1}$ does not give any Harker functions. A combination of symmetrical and unsymmetrical vectors can be used, however, in the conjugate peak pair method. It was first described 1952 [1] and later applied by Bezjak [2] and Buerger [3]. A description of the method is given by Buerger in *Vector Space* (p. 275).

The method works well for reasonably resolved Patterson functions but in complex cases it may be very difficult to find the single inversion peaks. It will then be necessary to work with areas of high values in the Patterson function and try to puzzle them together by trial and error.

Space-group $P 2_1 c$

The unsymmetrical vectors between two atoms r and s are:

$$x_r - x_s, y_r - y_s, z_r - z_s$$

$$x_r + x_s, y_r + y_s, z_r + z_s$$

$$x_r - x_s, \frac{1}{2} - (y_r + y_s), \frac{1}{2} + (z_r - z_s)$$

$$x_r + x_s, \frac{1}{2} - (y_r - y_s), \frac{1}{2} + (z_r + z_s)$$

if only the asymmetrical part of the Patterson function is considered. With a changed notation this can be written:

$$x_1, y_1, z_1$$

$$x_2, y_2, z_2$$

$$x_1, \frac{1}{2} - y_2, \frac{1}{2} + z_1$$

$$x_2, \frac{1}{2} - y_1, \frac{1}{2} + z_2.$$

If a well defined unsymmetrical peak x_1, y_1, z_1 is used as a starting point there must exist another peak $x_1, \frac{1}{2} - y_2, \frac{1}{2} + z_1$ on the line $P(x_1, y, \frac{1}{2} + z_1)$. This peak will determine y_2 and it remains to find x_2, y_2, z_2 and $x_2, \frac{1}{2} - y_1, \frac{1}{2} - z_2$ in the two sections $P(x, y_2, z)$ and $P(x, \frac{1}{2} - y_1, z)$. The whole procedure can be facilitated by the use of a minimum function if necessary. If one such quartet of vectors has been identified the corresponding inversion peaks can easily be calculated by combination of the vectors. The corresponding Harker and inversion peaks should be checked to have reasonable values but need not be resolved. One can try to combine all peaks in the Patterson function to quartets in the same way. This might be difficult in cases of large overlap (one well defined peak is enough for each quartet, however) and a usual image-seeking procedure with only two positions fixed (one quartet and eight atoms determined) will probably lead to a more rapid determination of the structure.

The extra possibility offered by the method is that only one well defined unsymmetrical peak with any multiplicity must be found instead of a single inversion peak.

If no good peak is found it might still be possible to start with an area of high values in the Patterson function and proceed in the same way.

Space-group $Pbca$

The unsymmetrical vectors between two atoms r and s are:

$$x_r - x_s, y_r - y_s, z_r - z_s$$

$$\frac{1}{2} - (x_r - x_s), \frac{1}{2} - (y_r + y_s), z_r + z_s$$

$$x_r + x_s, \frac{1}{2} - (y_r - y_s), \frac{1}{2} - (z_r + z_s)$$

$$\frac{1}{2} - (x_r + x_s), y_r + y_s, \frac{1}{2} - (z_r - z_s)$$

$$x_r + x_s, y_r + y_s, z_r + z_s$$

$$\frac{1}{2} - (x_r + x_s), \frac{1}{2} - (y_r - y_s), z_r - z_s$$

$$x_r - x_s, \frac{1}{2} - (y_r + y_s), \frac{1}{2} - (z_r - z_s)$$

$$\frac{1}{2} - (x_r - x_s), y_r - y_s, \frac{1}{2} - (z_r + z_s)$$

if only the asymmetrical part of the Patterson function is considered. With a changed notation this can be written:

$$\begin{aligned}
 &x_1, y_1, z_1 \\
 &\frac{1}{2} - x_1, \frac{1}{2} - y_2, z_2 \\
 &x_2, \frac{1}{2} - y_1, \frac{1}{2} - z_2 \\
 &\frac{1}{2} - x_2, y_2, \frac{1}{2} - z_1 \\
 &x_2, y_2, z_2 \\
 &\frac{1}{2} - x_2, \frac{1}{2} - y_1, z_1 \\
 &x_1, \frac{1}{2} - y_2, \frac{1}{2} - z_1 \\
 &\frac{1}{2} - x_1, y_1, \frac{1}{2} - z_2.
 \end{aligned}$$

If a well defined unsymmetrical peak x_1, y_1, z_1 can be found as a starting point there must exist another peak $x_1, \frac{1}{2} - y_2, \frac{1}{2} - z_1$ in $P(x_1, y, \frac{1}{2} - z_1)$ giving $\frac{1}{2} - y_2$. There are also peaks $\frac{1}{2} - x_1, y_1, \frac{1}{2} - z_2$ in $P(\frac{1}{2} - x_1, y_1, z)$ giving $\frac{1}{2} - z_2$, and $\frac{1}{2} - x_2, \frac{1}{2} - y_1, z_1$ in $P(x, \frac{1}{2} - y_1, z_1)$ giving $\frac{1}{2} - x_2$. The four remaining peaks will give extra checks on the solution. One can try to correlate all peaks in this way or an image-seeking procedure can be started as soon as one octet has been identified and the corresponding Harker and inversion peaks have been shown to have reasonable values.

In a recent structure determination [4] the method was applied to a case where no well defined peaks were found. It was possible, however, to correlate areas of high Patterson values in this way and thus reach a solution although the overlap was very large in the Harker functions.

The method outlined here can easily be extended to any space-group and the fundamental relations are implicitly given by Buerger in Vector Space (p. 116) but not further developed there. The method gives a convenient classification of all peaks also in cases where the method is not necessarily needed for the structure determination, and I have used it for that purpose during a long time.

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The error caused by inexact orientation in the determination of refractive indices of minerals by the immersion method

By MARIANNE GILLBERG

With 4 figures in the text

ABSTRACT

Diagrams have been constructed for the estimation of the required accuracy in grain orientation when determining the refractive indices of minerals. Three diagrams are presented, assuming maximum errors in refractive index of ± 0.001 , ± 0.0005 and ± 0.0001 , respectively.

For a refractive index, accuracy of 0.001, orientation error is of little importance compared with the other errors in routine determinations by the immersion method, at least for minerals with weak to strong birefringence. Only for minerals with very strong birefringence, e.g. many carbonates, need the orientation be perfect.

When an accuracy of 0.0005 is desired, the orientation must be almost perfect for minerals of strong and very strong birefringence. In the case of an accuracy of 0.0001, the orientation must be perfect except for minerals with very weak birefringence.

Introduction

Immersion liquids are generally used for routine determinations of refractive indices of minerals. Unfortunately, the immersion method suffers from several sources of error which restrict its applicability. For example, the liquids are very sensitive to small variations in temperature, even a small increase in which may cause a measureable decrease in refractive index. Most immersion liquids are unstable in the presence of air, and thus the composition might change during the operation. The refractive index is also a function of the wave-length (dispersion) with increasing wave-length the refractive index decreases. Even the refractive index of crystals varies with the wave-length, but the variation is considerably smaller than that found for liquids.

From these brief facts it is evident that the ordinary immersion method is not suitable for precision measurements. Micheelsen (1957), for example, states that the error is often ± 0.002 – 0.003 by the ordinary immersion method under ideal conditions, i.e. when the mineral grains are colorless, or nearly so, well-crystallized, free from inclusions and perfectly oriented.

The error caused by inexact orientation will be discussed in the following sections.

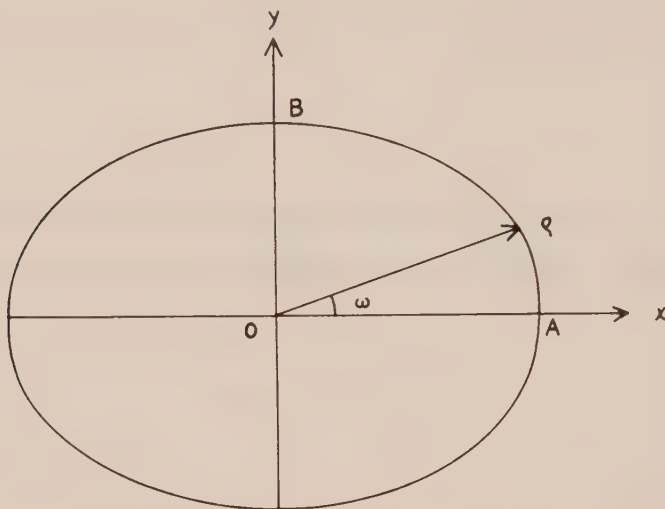


Fig. 1. Ellipse defined by the major axis, $OA=a$ is equal to n_y in the optical indicatrix, and radius vector ρ . The minor axis $=OB=b$.

Derivation of suitable formulas

The optical indicatrix for biaxial crystals may be described as a triaxial ellipsoid, whose three half-axes are n_y , n_β and n_x .

An auxiliary reference plane defined by the major axis, n_y , and the radius vector, ρ , will cut the ellipsoid, forming an ellipse. The angle between the major axis and the radius vector is called ω . In the ellipse thus formed we have (cf. fig. 1):

$$\begin{array}{lll} OA = n_y = a & OB = b & \rho = \text{radius vector} \\ n_x \leq b & n_y - b < n_y - n_x. & \end{array}$$

The equation of the ellipse expressed in polar coordinates can be written:

$$\frac{1}{\rho^2} - \frac{1}{a^2} = \left(\frac{1}{b^2} - \frac{1}{a^2} \right) \sin^2 \omega. \quad (1)$$

When $\omega = 0^\circ$, ρ has its maximum value $=a$, when $\omega = 90^\circ$, ρ has its minimum value $=b$.

We wish first to establish the error in determining $n_y = a$. We can write the radius vector, ρ , as $(a - \varepsilon)$, where ε is small compared to a . Then ε represents the error; for example, a value of 10^{-4} means that an error of 0.0001 is made in the determination of n_y .

Since it is practical to use variables which are simply related to measurable optical constants, we choose $x = \frac{a+b}{2}$ and $y = a-b$, the arithmetic mean of the refractive indices and the birefringence in the section, respectively.

To a first approximation, the left side of equation (1) can be written:

$$\frac{1}{\varrho^2} - \frac{1}{a^2} = \frac{1}{(a-\varepsilon)^2} - \frac{1}{a^2} \approx \frac{2\varepsilon}{a^3}.$$

Consequently, equation (1) becomes:

$$\frac{1}{b^2} - \frac{1}{a^2} = \frac{2\varepsilon}{a^3 \sin^2 \omega}. \quad (1a)$$

Introducing $A = \frac{\varepsilon}{\sin^2 \omega}$ and our variables x and y in equation (1a) we get:

$$\frac{A}{(2x+y)} = \frac{2xy}{(2x-y)^2}. \quad (2)$$

Solving (2) with regard to y we get after some simple calculations

$$y = \frac{-2x(A+x) + 2x \sqrt{(A+x)^2 + A(2x-A)}}{(2x-A)} \quad (3)$$

The other root to equation (3) has been discarded since we demand $y > 0$.

The expression under the root sign can be written as an infinite convergent series if $\left[\frac{A(2x-A)}{(A+x)^2} \right]^2 < 1$, compare formula on p. 88, Peirce (1929).

This expression can be rewritten as $\left[\frac{\frac{A}{x} \left(2 - \frac{A}{x} \right)}{\frac{A}{x} \left(2 + \frac{A}{x} \right) + 1} \right]^2$, if $\frac{A}{x} > 0$ it is obviously always smaller than 1.

$$y = \frac{x A}{(A+x)} - \frac{x A^2 (2x-A)}{4(A+x)^3} + \frac{x A^3 (2x-A)^2}{8(A+x)^5} - \frac{5x A^4 (2x-A)^3}{64(A+x)^7} + \dots \quad (4)$$

Each term in equation (4) can be expanded in a power series of A , if $\frac{A}{x} < 1$.

First term:

$$\frac{x A}{(A+x)} = \frac{A}{\left(1 + \frac{A}{x} \right)} = A \left(1 - \frac{A}{x} + \frac{A^2}{x^2} - \frac{A^3}{x^3} \dots \right) = A - \frac{A^2}{x} + \frac{A^3}{x^2} - \frac{A^4}{x^3} \dots$$

Second term:

$$\begin{aligned} \frac{x A^2 (2x-A)}{4(A+x)^3} &= \frac{A^2 (2x-A)}{4x^2 \left(1 + \frac{A}{x} \right)^3} = \frac{A^2 (2x-A)}{4x^2} \left(1 - \frac{3A}{x} + \frac{6A^2}{x^2} - \frac{10A^3}{x^3} \dots \right) = \\ &= \frac{A^2}{2x} - \frac{7A^3}{4x^2} + \frac{15A^4}{4x^3} - \frac{13A^5}{2x^4} \dots \end{aligned}$$

Third term:

$$\frac{x A^3 (2x - A)^2}{8(A + x)^5} = \frac{A^3 (2x - A)^2}{8x^4 \left(1 + \frac{A}{x}\right)^5} = \frac{A^3 (2x - A)^2}{8x^4} \left(1 - \frac{5A}{x} \dots\right) = \frac{A^3}{2x^2} - \frac{3A^4}{x^3} \dots$$

Fourth term:

$$\frac{5x A^4 (2x - A)^3}{64(A + x)^7} = \frac{5A^4 (2x - A)^3}{64x^6 \left(1 + \frac{A}{x}\right)^7} = \frac{5A^4 (2x - A)^3}{64x^6} \left(1 - \frac{7A}{x} \dots\right) = \frac{5A^4}{8x^3} \dots$$

If these terms are added we get the following power series:

$$y = A - \frac{3A^2}{2x} + \frac{13A^3}{4x^2} - \frac{67A^4}{8x^3} \dots \quad (5)$$

This equation has been used to obtain the numerical values used in the construction of the continuous lines in the diagrams, except for the smallest angles where equation (3) has been used.

We can proceed in a similar manner to calculate the corresponding error when n_α is measured. However, instead of using the reference plane defined by the radius vector and the major axis, we use a plane defined by the radius vector and the minor axis, obtaining a new ellipse. The angle between the minor axis and the radius vector is here denoted $(90^\circ - \varphi)$. We can write

$$\frac{1}{c^2} = \frac{1}{(d + \varepsilon)^2} = \frac{1}{d^2 \left(1 + \frac{\varepsilon}{d}\right)^2} = \frac{1}{d^2} \left(1 - \frac{2\varepsilon}{d} + \frac{3\varepsilon^2}{d^2} \dots\right) \approx \frac{1}{d^2} - \frac{2\varepsilon}{d^3}$$

where c = the major axis, d = the minor axis is equal to n_α .

Introducing this in the equation of type (1) for the new ellipse we get the following

$$\frac{1}{d^2} - \frac{2\varepsilon}{d^3} - \frac{1}{c^2} = \left(\frac{1}{d^2} - \frac{1}{c^2}\right) \sin^2 \varphi \quad (6)$$

or

$$\frac{1 - \sin^2 \varphi}{d^2} - \frac{2\varepsilon}{d^3} = \frac{1 - \sin^2 \varphi}{c^2}$$

$$\frac{1}{d^2} - \frac{1}{c^2} = \frac{2\varepsilon}{d^3 \cdot \cos^2 \varphi} \quad (7)$$

Now $\cos^2 \varphi = \sin^2 (90^\circ - \varphi)$.

Introducing $D = \frac{\varepsilon}{\sin^2 (90^\circ - \varphi)}$ and the variables $z = \frac{c + d}{2}$ and $u = c - d$ in (7) we get

$$\frac{2zu}{(2z + u)^2} = \frac{D}{(2z - u)} \quad (8)$$

Table 1. Maximum values of φ by determination of n_α .

ε	$\frac{c+d}{2}$	φ_{\max}	$c-d$
10^{-3}	1.5	87.04°	$1000 \cdot 10^{-3}$
	2.0	87.44°	$1333 \cdot 10^{-3}$
$5 \cdot 10^{-4}$	1.5	87.91°	$1000 \cdot 10^{-3}$
	2.0	88.19°	$1333 \cdot 10^{-3}$
10^{-4}	1.5	89.06°	$1000 \cdot 10^{-3}$
	2.0	89.19°	$1333 \cdot 10^{-3}$

Compare equation (2).

Solving equation (8) with regard to u

$$u = \frac{-2z(D-2z) - 2z\sqrt{(D-z)^2 - D(2z+D)}}{(2z+D)} \quad (9)$$

The other root to (8) has been discarded, since it gives impossible values of c and d . They must both be >1 . For the discriminant to be positive it is necessary that $(D-z)^2 - D(2z+D) \geq 0$ or $z \geq 4D$.

It means that u as a function of φ for given ε and z has a maximum for a value φ_m , which is determined by the equation $z-4D=0$ (cf. table 1). For $\varphi > \varphi_m$ the orientation errors are always smaller than the selected value of ε .

If we proceed in the same manner with equation (9) as with (3) we get:

$$u = D + \frac{3D^2}{2z} + \frac{13D^3}{4z^2} + \frac{67D^4}{8z^3} \dots \quad (10)$$

This series is convergent if $\left[\frac{D(2z+D)}{(D-z)^2} \right]^2 < 1$. This condition is satisfied because we have $0 < \frac{D}{z} < \frac{1}{4}$.

In comparison with equation (5) the second and the fourth term have a plus sign, both otherwise they are analogous. Choosing $D=A$, $z=x$ and $u=y$ the difference between (10) and (5) can be written:

$$y_\alpha - y_\gamma = \frac{3A^2}{x} + \frac{67A^4}{4x^3} \dots \quad (11)$$

For minerals with low birefringence the difference can be neglected. For those of higher birefringence compare the diagrams where dashed lines refer to n_α .

For uniaxial crystals the optical indicatrix is an ellipsoid of revolution. If the optical sign is positive, the refractive index for the ordinary ray is equal to n_α , independent of the orientation. The permitted deviation in the n_γ -determination can be derived from the diagrams. The corresponding is valid for negative crystals, but here the ordinary ray has the refractive index n_γ .

The diagrams and their use

As is well-known, grains with perfect orientation are often very difficult to find. Here we must take into account the time available to search for a suitably oriented grain. The main considerations in such a case are the required accuracy of the measurement, the birefringence and the refractive index. By using the diagrams it is readily seen how accurately a section must be oriented to obtain the desired accuracy.

The variables $(a+b)/2$ and $a-b$ used in the diagrams, are not the true optical constants, but refer to the auxiliary reference planes. This is not serious however. The difference between $(a+b)/2$ and $(n_\gamma + n_\alpha)/2$ can be neglected, because the function is almost horizontal and consequently almost independent of $(a+b)/2$. Furthermore we always have $n_\gamma - n_\alpha \geq a-b$, so the deviation angle read from the diagrams is always somewhat smaller than the permitted angle. Consequently this error is not important.

Three diagrams have been constructed. The first has been constructed under the assumption that the orientation error shall be less than 0.001 in the refractive index, the second and the third that the error shall be less than 0.0005 and 0.0001, respectively.

From diagram A it appears that the orientation error is of no importance in routine determinations by the immersion method, except for minerals with very strong birefringence, e.g. many carbonates and rutile. In determining n_γ of an amphibole, such as hornblende ($n_\gamma - n_\alpha = 19.26 \cdot 10^{-3}$) the grain might be turned $10-11^\circ$ from the ideal orientation, without any influence on the orientation error. In such a case one should not spend too much time to find a grain with perfect orientation. For tremolite ($n_\gamma - n_\alpha = 22.27 \cdot 10^{-3}$) and diopside ($n_\gamma - n_\alpha = 29.31 \cdot 10^{-3}$) a deviation of about 10° from the ideal orientation can be tolerated. For minerals with weak birefringence such as kaolinite and mellite, for example, the tolerance limit is about $20-25^\circ$.

On the other hand, if one wishes to measure the refractive index with an orientation error of less than 0.0005, difficulties begin to arise. For example, sphene ($n_\gamma - n_\alpha = 92.141 \cdot 10^{-3}$) can only be measured with this accuracy if the orientation is exact within $3-4^\circ$. This accuracy of orientation cannot be obtained by interference figures alone, so in this case the use of a universal stage is necessary. For minerals with weak birefringence such as beryl ($n_\gamma - n_\alpha = 4.8 \cdot 10^{-3}$) however, the deviation angle might be $15-20^\circ$ (see diagram B).

It is possible to determine the refractive index with an accuracy of 0.0001 with the so-called "glass-method" (Micheelsen 1957). From diagram C it is evident that minerals with moderate to strong birefringence require perfect orientation. If this condition is not met, the errors caused by inexact orientation may be considerably larger than those caused by other errors. Even for a mineral with weak birefringence such as heulandite ($n_\gamma - n_\alpha = 7 \cdot 10^{-3}$), for instance, the maximum permitted deviation angle is only 7° .

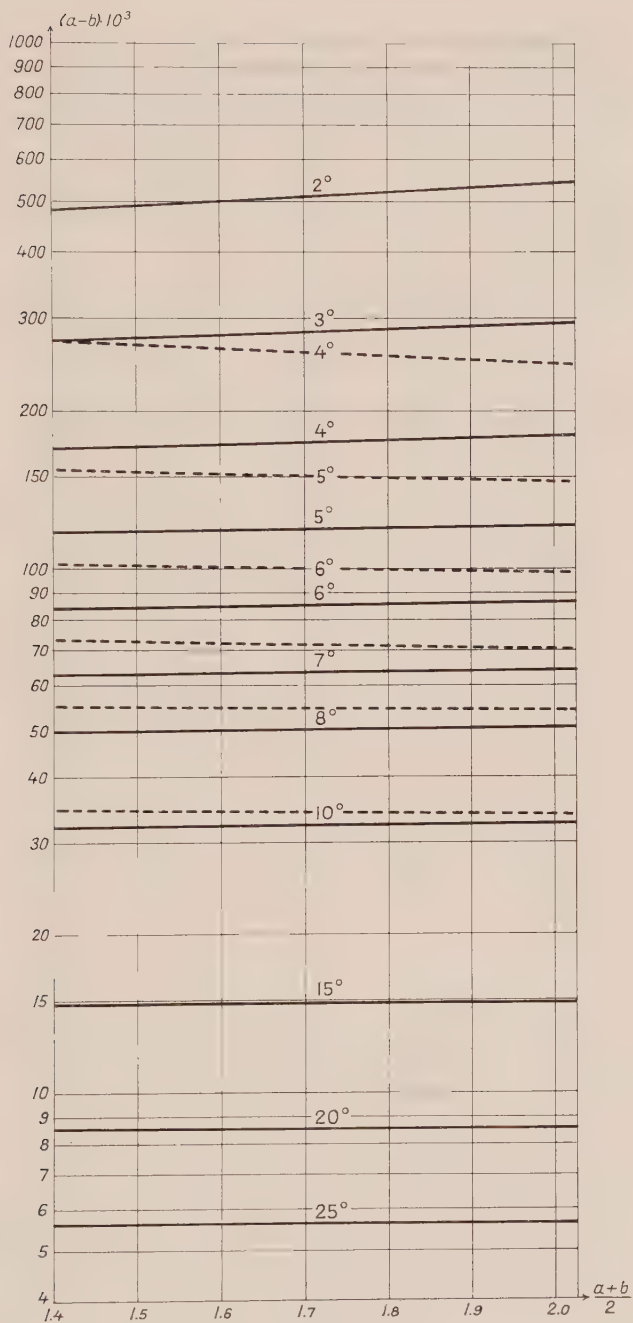


Fig. 2. Diagram A constructed for an orientation error of 0.001. $a-b$ and $(a+b)/2$ represent the birefringence and the arithmetic mean of the refractive indices of the section, respectively. The continuous lines refer to n_γ - and the dashed lines to n_α -determinations.

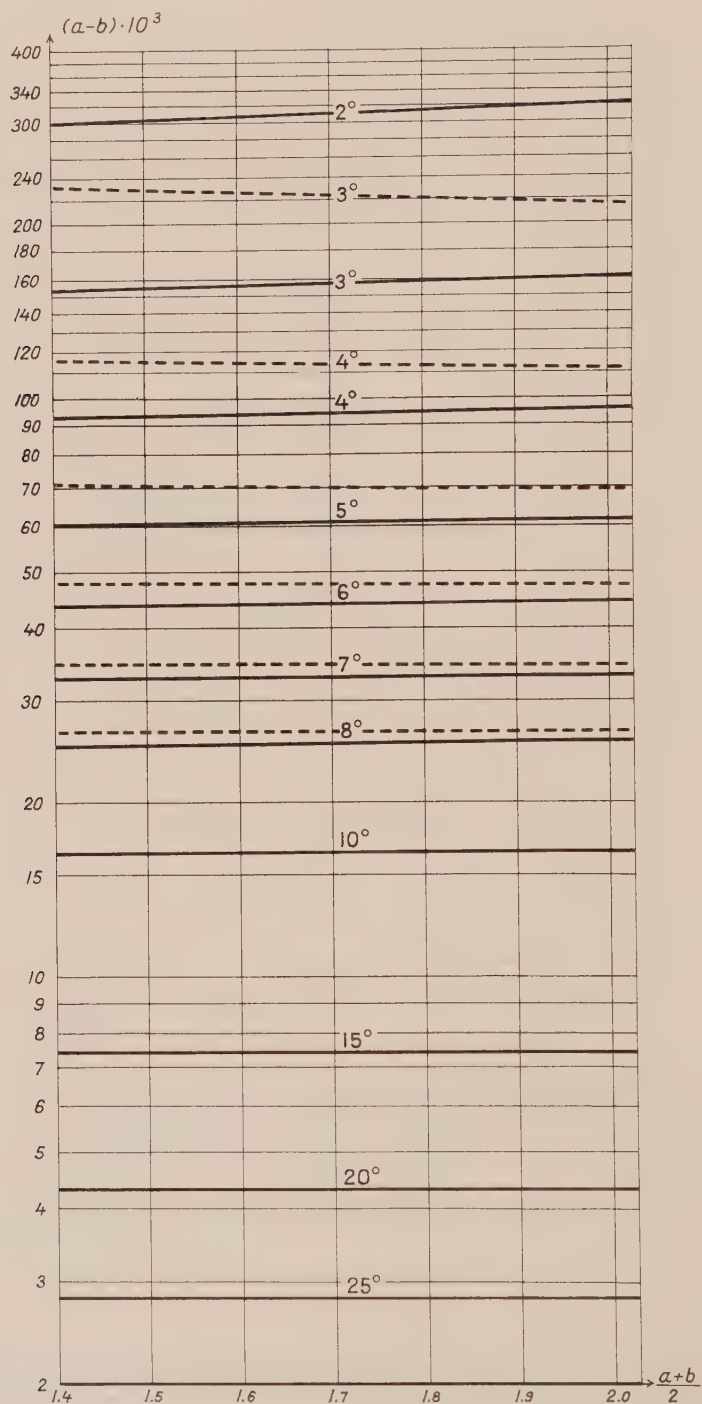


Fig. 3. Diagram B constructed for an orientation error of 0.0005.

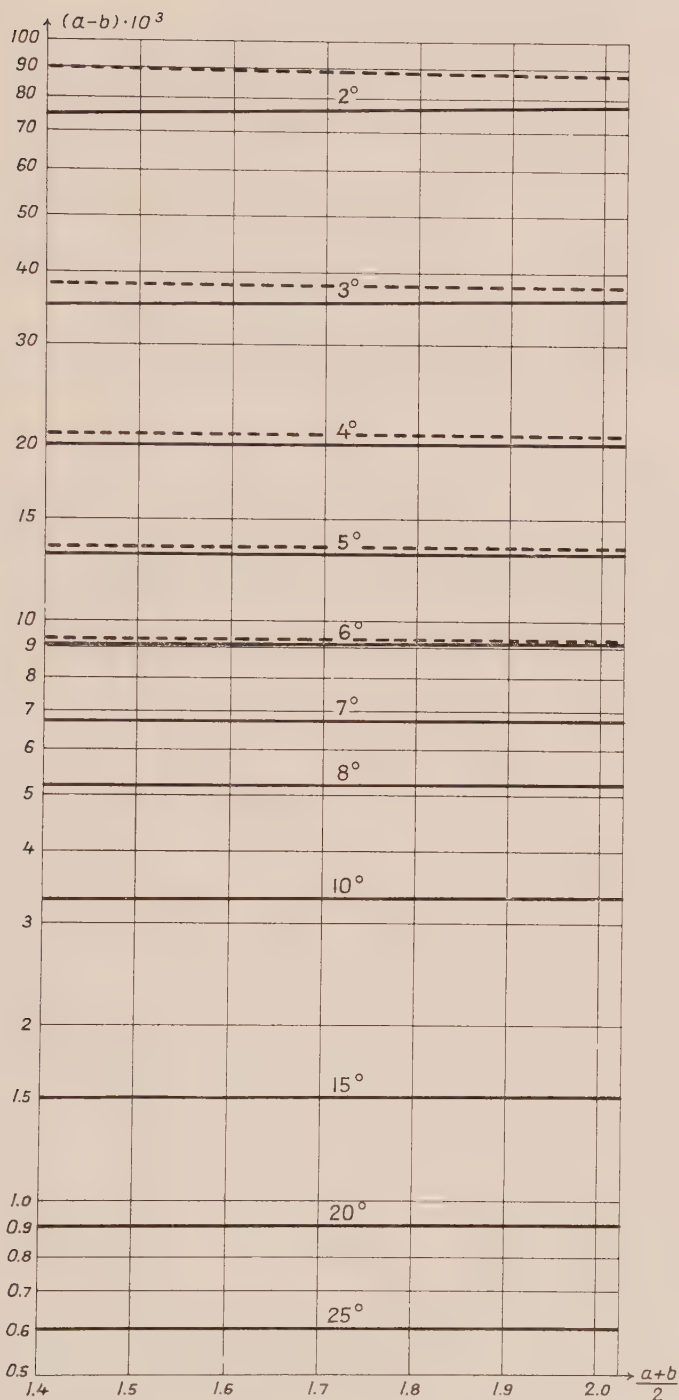


Fig. 4. Diagram C constructed for an orientation error of 0.0001.

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Borengite

A new ultra-potassic rock from Alnö Island

By HARRY VON ECKERMANN

With 12 figures in the text

A few years ago a new local road was built between the villages of Nacka, situated on the northern shore of Alnö Island, and Nysäter on the main western road about one kilometre north of the church of Alnö parish. Passing immediately to the west of Båräng farm the road cuts through the projecting spur of a rocky hill north of the farm (Fig. 1). The gneiss granite of the hill is intersected by a dike, varying from 70 to 90 cm in width and running in a south-south-westerly direction with a northerly dip of 70° (Fig. 2). I have named the dike-rock *borengite*, an anglicization of Båräng.

At a distance the dike is very similar to the reddish quartz-porphyric spotty Jotnian dikes with dark quartz phenocrysts (so-called "Sundsvall porphyries") occurring on the mainland west of Alnö and associated with the Rödö Jotnian region east of Alnö Island. At close quarters, however, the dark spots are found to consist of purple fluorite surrounded by greenish and (or) whitish rims. The spots are fairly uniformly scattered in a very fine-grained rock of reddish-brown colour (Fig. 3).

Microscopically the ground-mass shows a beautiful trachytic flow texture with no appreciable amount of glassy residue. The ground consists essentially of minute feldspar laths with some degree of parallel disposition accentuating the flow. Their length averages 0.025–0.075 mm and their extinction 3–5 degrees. Occasionally the feldspar laths are set in a still finer grained ground of colourless flakes of probably hydrosericitic composition. Between the feldspar laths are small grains of carbonate, pyrite, ilmenite (pseudomorphs of perowskite), hematite and iron hydroxides—the latter responsible for the colouring of the rock (Figs. 4 and 10).

Within the trachytic ground-mass occurs sparsely well crystallized larger laths and an older generation of feldspar, averaging $(0.1\text{--}0.2) \times (0.3\text{--}1.0)$ mm. They are partly Carlsbader-twinned and generally strongly pigmented by iron hydroxides. While the small size of the laths of the ground-mass does not allow of any optical measurements, these larger crystals are measurable, although strong pigmentation and part sericitization makes the optical data somewhat approximate. The following characteristics were found: $n_x = 1.517 \pm 0.002$, $n_y = 1.524 \pm 0.002$, $(n_y - n_x) = 0.007$, $a/\alpha = 3\text{--}5^\circ$, $2V = -71^\circ \pm 2^\circ$. On account of the pigmentation all determinations were made at $\lambda = 550$. The feldspar seems to be an orthoclase (Figs. 5, 6 and 7).

Besides this feldspar, rectangular or hexagonal pseudomorphs—now consisting of sericite and possibly some natrolite—are sparsely scattered within the ground-mass. Although the presence of natrolite could not be confirmed microscopically, the



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Fig. 1. Site of dike, indicated by circle North of Båräng. Scale: 1:100,000.

crystal shapes hardly allow of any other deduction than that of a primarily crystallized nepheline (Fig. 7). Professor Th. G. Sahama has kindly undertaken an X-ray determination of the feldspar of the ground-mass, including the few older feldspar phenocrysts, and has found it to be triclinic and strongly so, approaching that of microcline. None of the characteristic twinning of microcline, however, is observable microscopically. Professor Sahama also raises the question whether some of the rectangular sericitized pseudomorphs could have been feldspars representing a transition from microcline into low-temperature sanidine (Figs. 4 and 12).

Fairly large apatite crystals of up to $1\frac{1}{2}$ mm in length also occur fairly sparsely as phenocrysts. They are generally unaltered. A couple of square pseudomorphs were observed, which contained not only sericitic mica but some carbonate as well. This may indicate a calcium content of the original mineral, either feldspar or nepheline. However, since the carbonate occurs too as narrow streaks or as isolated vug-like spots in the ground-mass, the possibility of a later metasomatic infiltration of carbonate in the pseudomorphs should not be overlooked (Figs. 8 and 12).

Microscopical examination of the dark, dominantly greenish spots of the rock confirms the purple colour of some of the megascopically observable fluorite, while some of it is almost colourless. Generally, the fluorite is associated with carbonate, a colourless, flaky mineral of sericitic appearance and nicely crystallized pyrites. The maximum refringence of the carbonate seems to vary, but it is generally higher than 1.66, indicating a somewhat dolomitic composition. Generally the carbonate occupies the rims of the spots and the sericite the centres. The fluorite occurs mostly in the centres but may also be observed as spots arranged concentrically within the carbonate, or even as late fissure-filling running across a spot (Figs. 5, 9, 10 and 11).



Fig. 2. The borengite dike in the eastern wall of the road-cutting.

Megascopically one would deem the green colour of the spots to be due to the presence of some chloritic mineral, but actually it comes almost exclusively from the weak bluish-green tint of the carbonate, which against the brown "background" of the rock itself appears greenish. Diluted hydrochloric acid dissolves the "content" of the spots leaving the colourless micaceous flakes among which a few greyish ones may rarely be found. To Olof Gabrielson, Lic.Sc., I am indebted for an X-ray investigation of the sericite-like mineral, which showed a pattern closely related to that of normal muscovite and, in consequence, may be taken to be sericite. A determination of the refractive indices resulted in $n_y = 1.592 \pm 0.003$ and $n_z = 1.553 \pm 0.003$, or slightly higher than pure muscovite, containing no iron.

The fluorite-carbonate-sericite spots are probably vesicles or vugs, within which the minerals crystallized during the later stages of the consolidation of the dike. Around them the iron pigmentation of the rock is reduced, as evidenced by lighter coloured zones, where some late-magmatic metasomatic exchange has taken place

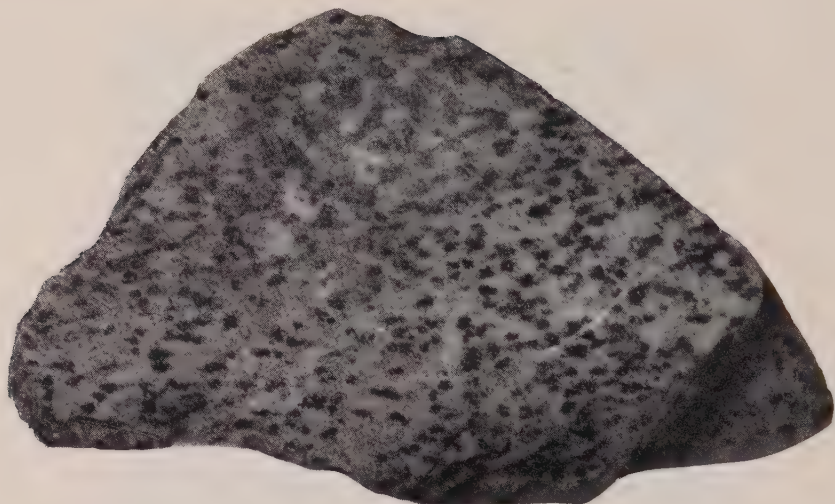


Fig. 3. Borengite. The blurred upper part with no dark spots represents a part of the original weathered surface where the carbonate and the fluorite of the vesicles have been dissolved. Half natural size.



Fig. 4. The trachytic texture of borengite. At the bottom a nepheline- or sanidine-(?) crystal altered into sericite and natrolite(?). $\times 30$.

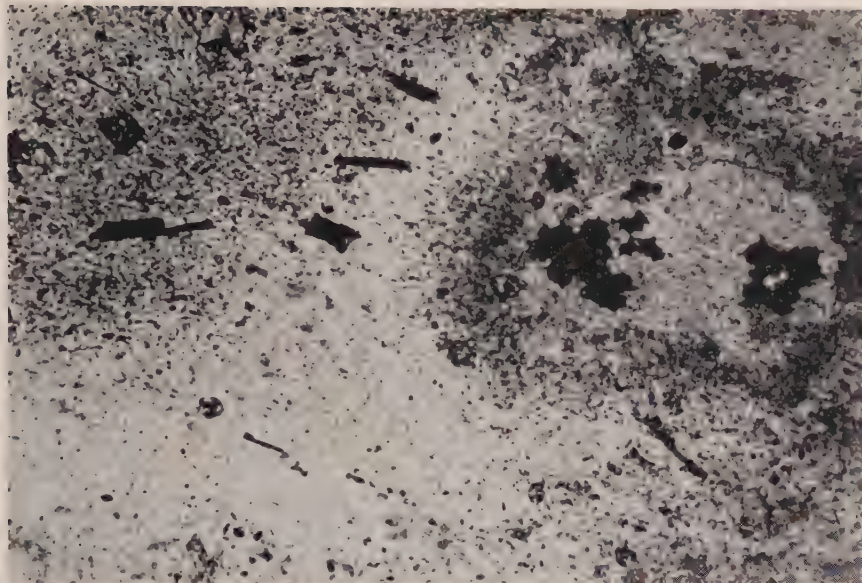


Fig. 5. Bleached zone around vesicle. The dark rim of the vesicle is carbonate and the black spots in the centre fluorite. To the upper left four strongly pigmented older feldspars (black) and a pseudomorph of perowskite. $\times 20$.

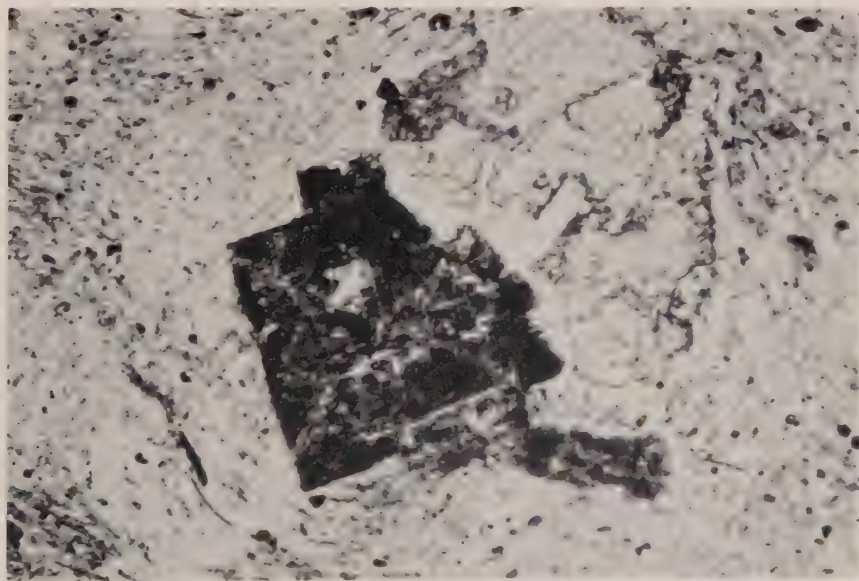


Fig. 6. Within the potassic ground-mass lies a strongly pigmented feldspar phenocryst (black) separated by sericite (white) from irregular grains of fluorite (light grey) to the upper right. The feldspar is corroded towards the sericite. $\times 30$.

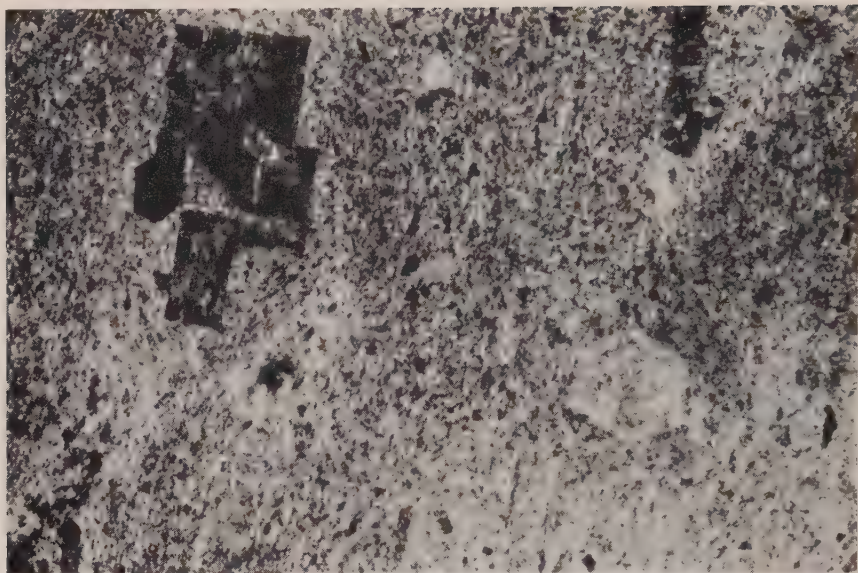


Fig. 7. At the top of the picture feldspar phenocrysts (black) and to the right at the bottom an altered nepheline crystal. $\times 20$.

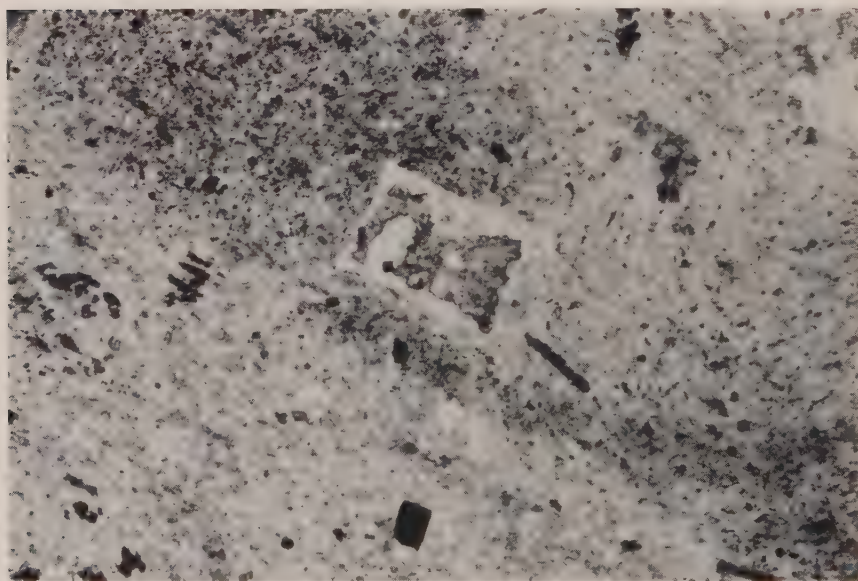


Fig. 8. Carbonate within a sericitized rectangular pseudomorph. $\times 20$.

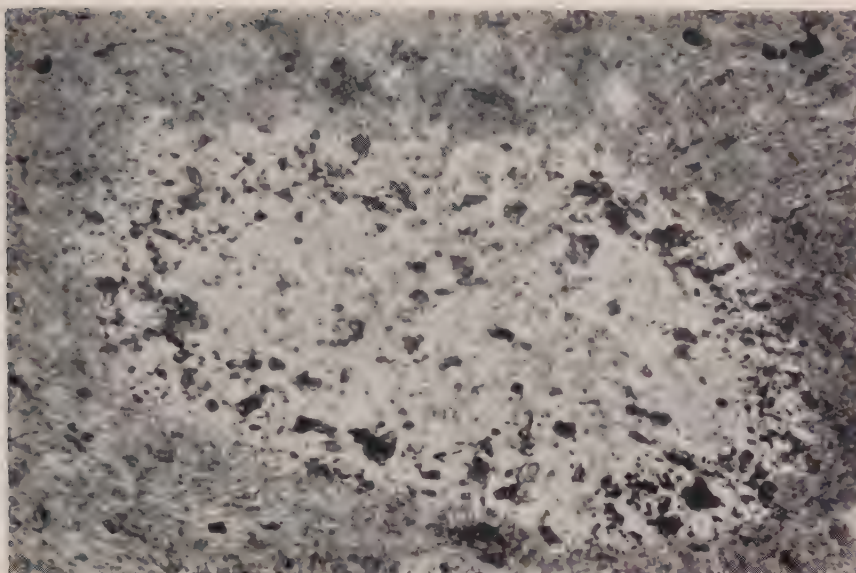


Fig. 9. A vesicle with a rim of carbonate (dark grey) and fluorite (black) around the sericite, $\times 15$.



Fig. 10. At the lower right a vesicle containing sericite with occasional small carbonate grains and an aggregate of purple fluorite (dark grey), $\times 25$.

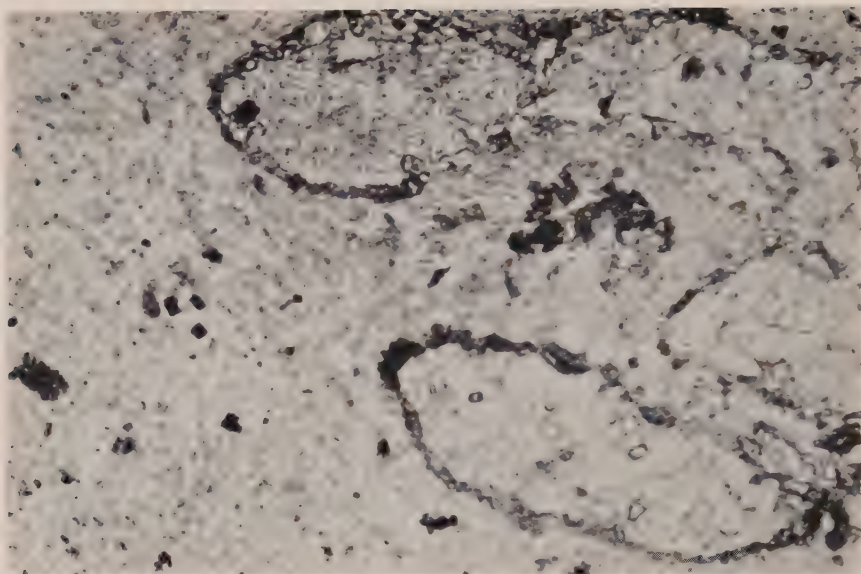


Fig. 11. Almost colourless fluorite with purplish rims (black and dark grey) within a "secondary" vesicle intersecting another one (outside the picture to the right) and continuing in the ground-mass. Rectangular black crystals are pyrites, the dark grey area in the ground-mass between the two "arms" of the fluorite-vesicle is carbonate. $\times 30$.

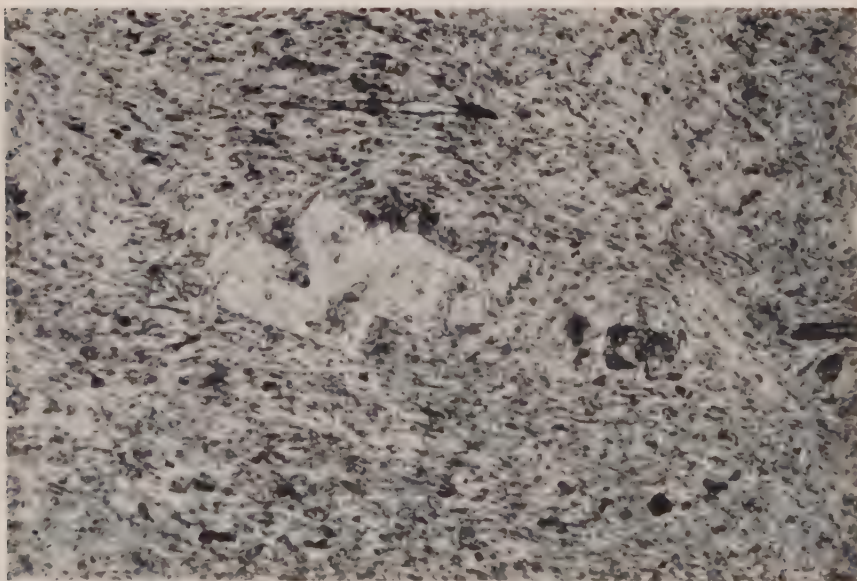


Fig. 12. In the middle a sericitized pseudomorph. Above it an apatite crystal and to the right one of the frequent carbonate spots (dark grey) occurring in the ground-mass. $\times 25$.

Table 1. Analysis of an average sample of Borengite, taken at every fifth centimetre across the dike.

Analyst: R. Blix.

	Weight (%)	Mol. prop. × 100	Norm	Mode	Weight (%)	Niggli's system
SiO ₂	56.96	94.84	q 1.91	Potassic feldspar	75.6	si 224
CO ₂	1.47	3.34	or 83.19	(Or ₉₈ Ab ₂)		qz + 20
TiO ₂	0.26	0.33	ab 1.52	Sericitic mica	17.8	co ₂ 7.90
Al ₂ O ₃	20.24	19.86	c 4.71	Carbonate	3.4	ti 0.78
Fe ₂ O ₃	1.11	0.70	Σ sal 91.33	(cc ₇₂ mg _{t19} sd _{t1})		al 47
FeO	1.18	1.64		Iron hydroxides	1.1	fm 9
MnO	0.07	0.10	hy 0.21	Fluorite	0.9	c 8
MgO	0.29	0.72	mt 1.61	Ilmenite	0.5	alk 36
CaO	1.93	3.44	il 0.50	Pyrite	0.6	mg 0.18
BaO	0.13	0.09	pr 0.55	Apatite	0.1	c/fm 0.92
SrO	0.01	0.01	ap 0.13		100.0	k 0.98
Na ₂ O	0.18	0.29	fr 0.92			p 0.09
K ₂ O	14.08	14.95	cc 2.52			h 16.42
P ₂ O ₅	0.06	0.04	mgt 0.61			o 0.37
F	0.37	1.95	sd _t 0.22			w 0.45
S	0.26	0.81	Σ fem 7.27			f ₂ 2.25
H ₂ O ^{+105°}	1.25	6.94	H ₂ O 1.61			s ₂ 0.94
H ₂ O ^{-105°}	0.36					Q 36.6
	100.21		100.21			L 59.0
-O=	0.30					M 4.4
	99.91					π 0.10
						γ 0.00
						α -1.83
						μ 0.18

Quantitative system: I:5:1:1; Rang Nordmarkose. Sp. gr. $\frac{20}{4}$ C°: 2.752.

between the gaseous matter within the vesicles and the surrounding rock-walls (Fig. 5).

To R. Blix, Lic. Sc., I owe a debt of gratitude for the great pains he took in determining the true F,CO₂ and H₂O contents of this new and remarkable dike-rock when performing the analysis, given in Table 1. These contents were checked by repeated analyses.

The analysis shows a quite unique composition, which as far as I have been able to ascertain has no counterpart among up to now known rocks of magmatic habit. According to the C.I.P.W. classification it falls within the rang "Nordmarkose", but no true example of any rock in subrang "I" has so far been given. The orthoclasite from Alaska, tentatively mentioned by H. S. Washington (1917), contains 73.39 or and 9.43 ab and should actually be placed in II.5.1.2 instead. Albert Johannsen gives in his classification (1931) no rock similar to the borengite. The closest approach is the kamperite (Brögger, 1921) which contains 10.16 % K₂O but as much as 2.27 % Na₂O and 4.17 % MgO. Still more potassic is the bostonite from The Haven, Swona, Orkney, which contains 20.91 % Al₂O₃, 11.34 % K₂O and 1.66 Na₂O, and which is described as containing "porphyric crystals of sanidine and anorthoclase in a plexus of elongated crystals of orthoclase arranged with some parallelism (Summary Progress Geol. Survey of Great Britain 1928)". The potassic kanzibite of the Kivi region in

Belgian Congo, to which Professor Sahama drew my attention, displays certain similarities, such as the relationship to carbonatites, but does not contain more than the half of the percentage of K_2O of the borengite.

In order to facilitate the determination and calculation of the mode of the rock, 12 thin slides from samples taken simultaneously with the average analysis sample were measured geometrically. The average worked out at 78 % feldspar, 14 % sericitic mica, 5 % carbonate and fluorite and a rest of 3 %. A calculation made from the analysis gave somewhat different values. It was based on the following plausible presumptions:

- (1) all barium and sodium is included in the feldspar;
- (2) all magnesium occurs as carbonate;
- (3) iron in excess of that occurring in siderite, ilmenite and pyrite is divided between the sericite (Fe^{++}) and the pigmenting hydrates and hematite (Fe^{++}); and
- (4) the CO_2 and H_2O values are correct and the total amount has to be accounted for.

This leads to the Mode, given in Table I. The albite content of the feldspar is, of course, a maximum value, which decreases in case the sodium is evenly distributed between the feldspar and the sericite or occurs as natrolite. The composition of the dominantly calcitic carbonate agrees with the previously determined higher refringence, and that of the sericitic mica works out at: $(K_{0.27}H_{0.73})_2(Al_{0.92}Fe_{0.08})_2Si_2O_8$.

Now the question is by what process such a unique rock as the borengite could have originated. Doubtless, it is no direct differentiate of the CO_2 -rich kimberlite or melilitite which constitute the mother magma of the Alnö intrusion, even if there is an intimate connection between the two. I believe its origin to be the mobilized fenite around the intrusion, even if the ultra-potassic feldspar does not agree very well with that of the other rheomorphic magmas. The potassic feldspar of the latter has so far always been found to be soda-orthoclase, the percentage of Na_2O never falling below 8 % of total alkalies according to a still unpublished series of analyses. This is also shown by the rock analyses, as for instance that of the Nordmarkitic fenite, Analysis No. 12 of my Alnö Memoir (S.G.U. Ser. Ca No. 36, 1948), where the Niggli values $Q = 38.2$, $L = 55.6$ and $M = 6.2$ do not differ much from those of the borengite, but where k is only 0.56 against 0.98.

I am not able at present to advance any tenable theory explaining the formation of the ultra-potassic feldspar. The rare nepheline pseudomorphs may suggest a squeezing out of the "borengite magma" from a crystal-mush of nepheline, but this leaves one to explain how the crystallization of nepheline could result in a purely potassic rest-solution. Unfortunately, no connecting link between the borengite and the other reomorphic Alnö rocks, which could supply a clue for further theorizing, has so far been found. As the most potassic rock of magmatic habit known today in the world, borengite is not only quite unique but its genesis is also a challenge to geochemists.

Tryckt den 10 augusti 1960

Uppsala 1960. Almqvist & Wiksells Boktryckeri AB

Read 25 May 1960

Boulders of volcanic breccia at the Sälskär shoals north of Alnö Island

By HARRY VON ECKERMANN

With 10 figures in the text

At some time during the breaking-up of the ice in the winters of 1949–1955, one large and several smaller boulders were pushed up from the depths of the sea on to the rocky shoals at Sälskär north of Alnö Island and NNW of Säg-holmen Island (cf. ref. [1], p. 72, Fig 15, and Fig. 2 of this paper). I brought one of the smaller boulders home for investigation and had it cut in two right through the centre (Fig. 1).

I have enjoyed a generous grant from the Swedish State Research Board and the kind assistance of Mr. A. Aaremäe, who performed the chemical analyses, and of Mr. E. Welin, Lic.Sc., who took the autoradiographs. I express my hearty thanks to them as well as to the head of the prospecting department of the Swedish Atom Energy Co. Ltd., Mr. Carl Mårtensson, through whose good offices I obtained a spectral analysis of the matrix of the breccia. All photographs are taken by the author.

The breccia consists of more or less rounded chips and fragments of sövite in a matrix of apatite, calcite and mica. This matrix also contains very nicely rounded, boulder-like inclusions of kimberlites, melilitites and single olivines or olivine aggregates.

The sövite is of a composition and of a general appearance not previously observed either within the alkaline area of Alnö Island, or in the two deep drill-hole soundings, described by the author in his Alnö Memoir ([1], p. 59). The presence of about 1% SrO and only 0.15% BaO is remarkable as it reverses the Ba/Sr ratio established during my earlier surveys (cf. ref. [2], p. 368). As neither strontianite nor emmonite have been observed microscopically, the strontium carbonate must occur intermixed with the other carbonates. A large percentage of SrO is previously known to exist in a narrow cone-sheet dike on the mainland only (cf. ref. [1], p. 121, analysis 97). This dike emanates from one of the fairly deep-seated fractioning centres of the volcanic conduit of the Alnö intrusion. The sövite of the breccia may therefore be assumed to have been brought up from considerably greater depths than the normal sövite on the island—a depth at which the magnesite component of the dolomitic carbonate has not yet been totally decomposed by silification.

The sövite is partly a very pure homogeneous carbonate (Fig. 3), partly slightly “banded”, as illustrated in Figs. 1 and 2. The “bands” consist of apatite, mica

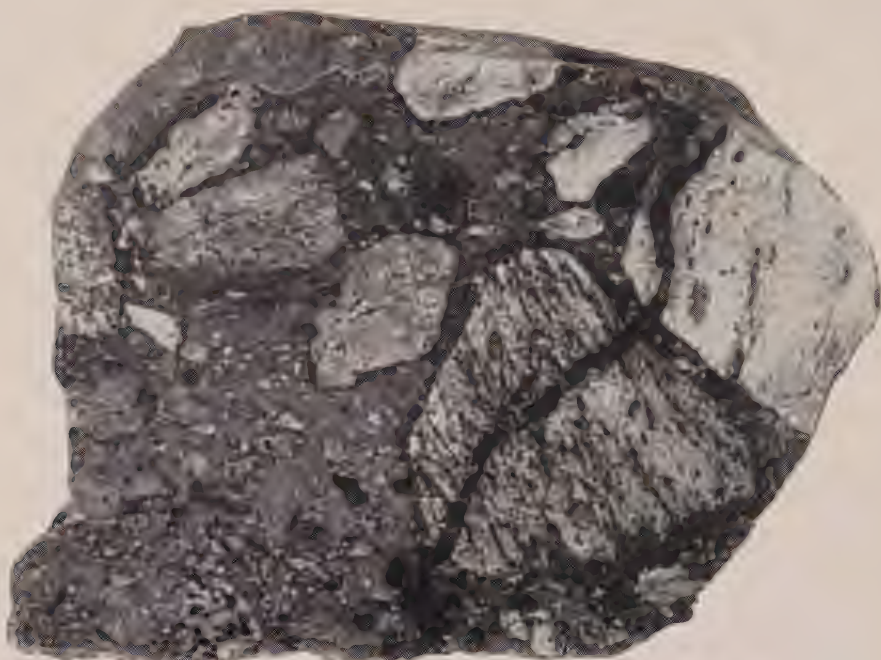


Fig. 1. Cross section of a breccia boulder, One-third of natural size.



Fig. 2. Two breccia boulders on the Sälskär shoals.

Analysis No. 1. Sövite fragments in breccia boulders at Sälskär.

Analyst: A. Aaremäe.

	Weight %	Mol. prop. × 100	Mode	%
SiO ₂	0.98	1.63	Carbonate	88.3
CO ₂	38.81	88.21	(cc92.5 mgt _{4.3} sdt _{3.2} etc.)	
TiO ₂	0.04	0.05		
Al ₂ O ₃	2.91	2.86	Mica	2.2
Fe ₂ O ₃	0.07	0.04	Ores	0.9
FeO	0.20	0.96	Apatite	6.2
MnO	2.20	0.28	Diaspor(?)	2.4
MgO	2.03	5.04		
CaO	49.26	87.84		100.0
BaO	0.15	0.10		
SrO	0.99	0.96		
Na ₂ O	0.02	0.03		
K ₂ O	0.22	0.87		
P ₂ O ₅	2.69	1.89		
S	0.28	0.87		
H ₂ O ^{+110°}	0.44	2.44		
H ₂ O ^{-110°}	0.19			
	99.97			
-O=S	0.10			
	99.87			

and ores, the latter being mostly pyrite and magnetite. The mica is of a very light brown colour and probably phlogopitic. A mineral also occurs, in tiny colourless scales, which is not determinable by microscopy. According to the calculated mode of Analysis No. 1 it may be diaspor. There is not enough water for the formation of gibbsite.

The matrix exhibits a more or less developed coarse flow texture, emphasized by the orientation of the apatite prisms and to some extent by the mica. (Figs. 4 and 5.) The latter has brown kernels and colourless rims and its composition changes accordingly from biotitic to sericitic. The carbonate of the matrix is a pure calcite and the grain varies considerably in size as opposed to the generally more even grained sövite.

The dark rounded inclusions within the matrix represent a great variety of basic rocks, mostly of kimberlitic compositions with serpentized and (or) fresh olivines, with or without pyroxenes and with more or less melilite. (Figs. 6 and 7.) Single crystals or aggregates of generally fresh olivines are surrounded by dark, rounded rims of melilite, intermixed with grains of magnetite, perovskite and pyrite. (Fig. 8.) The composition of the olivine is forsteritic and in some cases hyalosideritic.

The breccia is strongly radioactive, the Hoffman scaler running up to 8-900 counts/min against a background of about 40. The radioactivity is mainly confined to the matrix, and autoradiographs (Fig. 10) show it to be fairly evenly distributed throughout the rock. Dark areas represent no radioactive crystals of olivine or calcite. The radioactivity comes from small, mostly cubic crystals of high refraction and dark yellow or brown colour (Figs. 5 and 9). They have

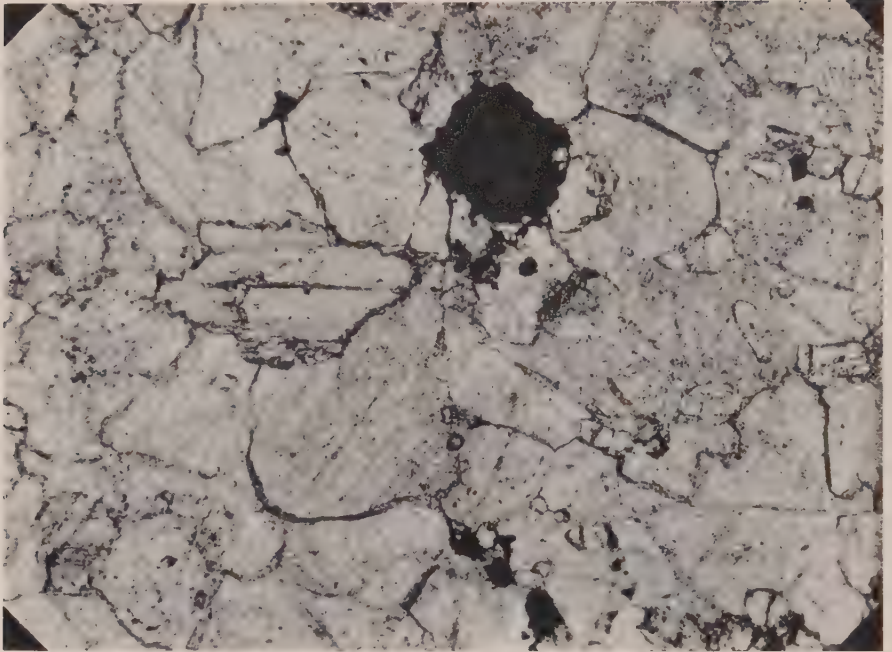


Fig. 3. Sövite in the Sölskär breccia boulders. To the upper right magnetite (black) and below to the left a phlogopite crystal. To the right and at the bottom apatites. Ordinary light. $\times 40$.

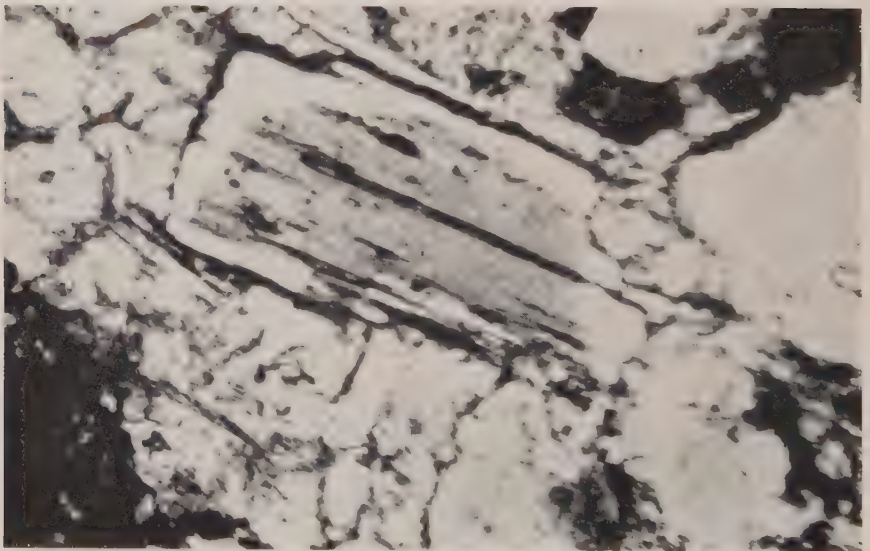


Fig. 4. Biotite (grey) with sericitic rims (white), surrounded by calcite. Ordinary light. $\times 60$.

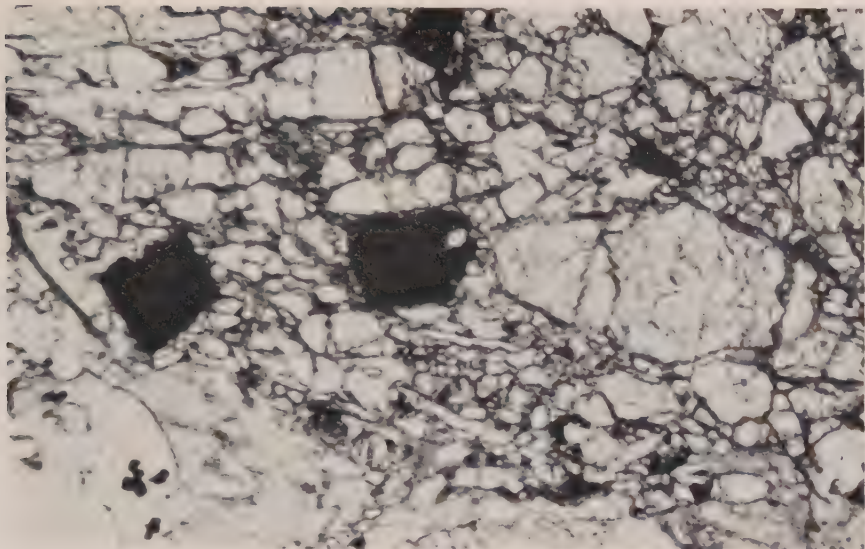


Fig. 5. Apatite (light grey with darker contours) and three, presumably pyrochlore crystals. Ordinary light. $\times 50$.

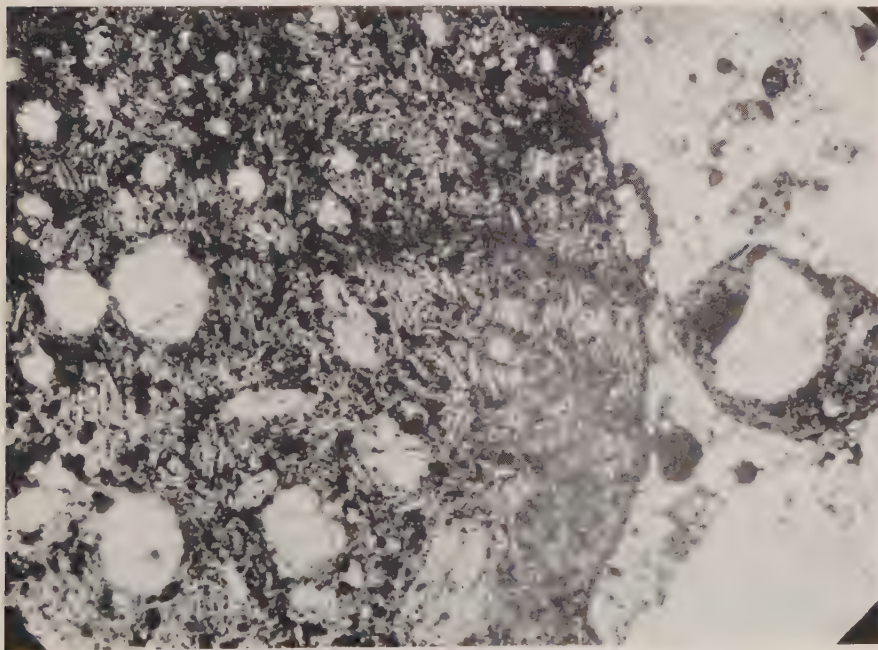


Fig. 6. Fragment of olivine-melilitite in breccia boulder. Rounded olivines, mostly serpentinized, in a melilitite ground-mass to the left. To the right fresh olivine surrounded by melilitite in a matrix of apatite and calcite. Ordinary light. $\times 40$.



Fig. 7. Partly serpentinized olivine crystal in kimberlite. Above the crystal a grain of pyroxene. To the lower left yellowish brown biotite. Ordinary light. $\times 50$.

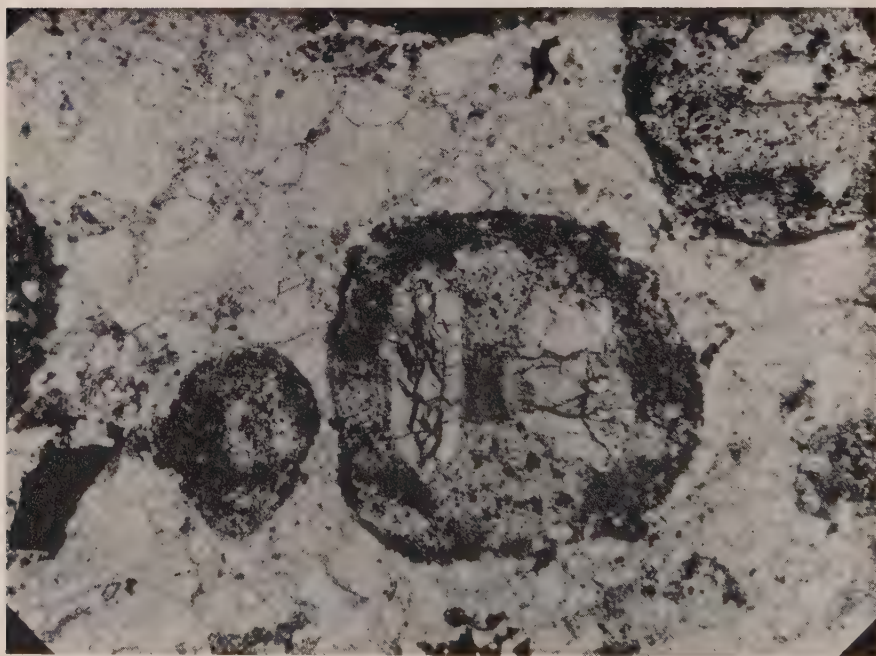


Fig. 8. Olivine crystals surrounded by melilite rims. The ground-mass is calcite and small apatites. The small dark more or less square spots are radioactive pyrochlore. Ordinary light. $\times 40$.

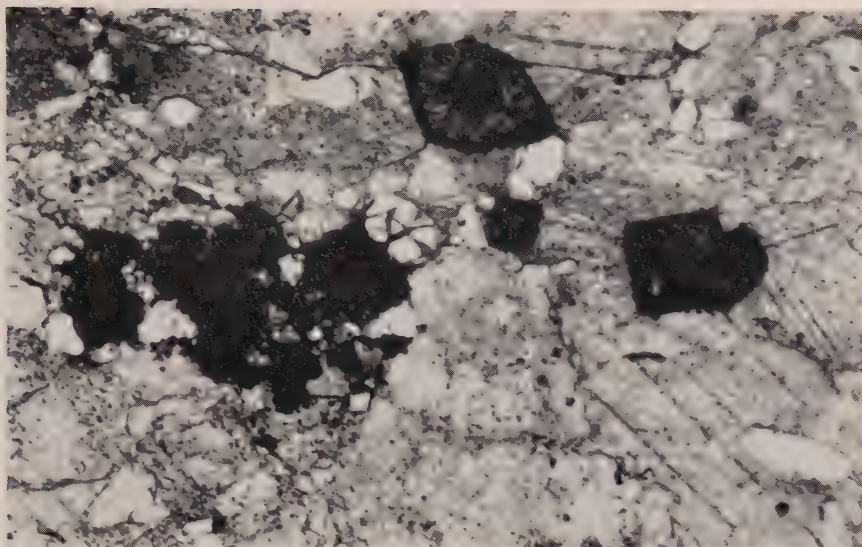


Fig. 9. Radioactive yellowish brown pyrochlore(?) (black and dark grey) in a matrix of calcite (light grey) and apatite (white). Ordinary light. $\times 60$.

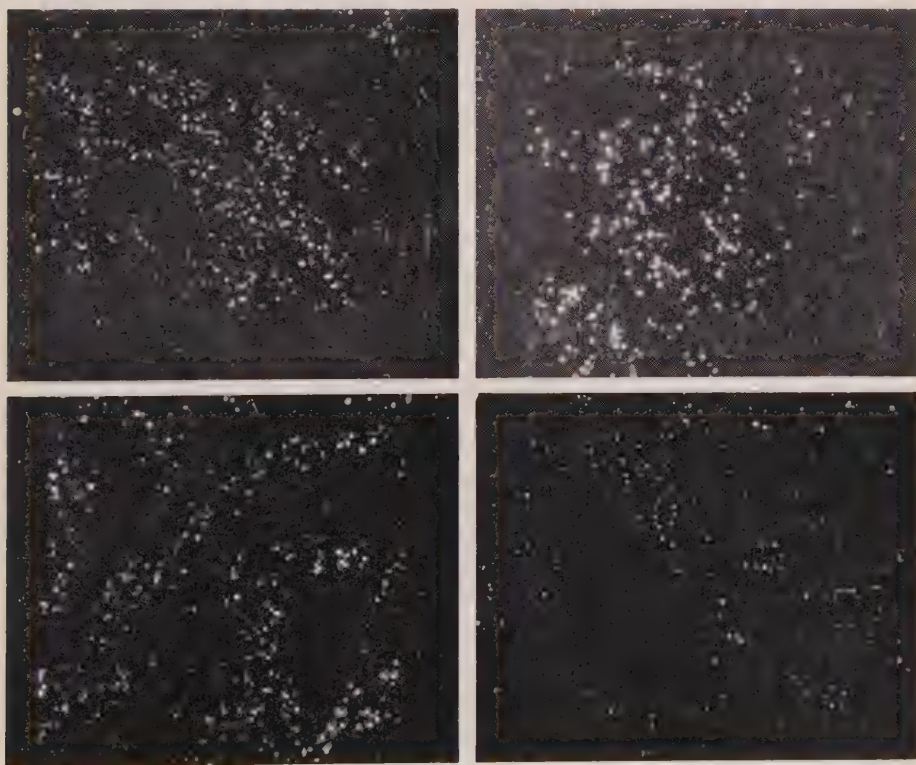


Fig. 10. Autoradiographs of the matrix of Sölskär breccia.

Analysis No. 2. Average sample of matrix between sövite fragments in breccia boulders at Sölskär.

Analyst: A. Aaremäe.

	Weight %	Mol. prop. × 100	Mode	%
SiO ₂	19.24	21.55	Calcite	49.3
CO ₂	21.64	49.18	Olivine and olivine pseudomorphs	13.6
TiO ₂	1.12	1.40	Mica	11.1
Al ₂ O ₃	5.27	5.17	Apatite	7.6
Fe ₂ O ₃	4.45	2.79	Magnetite	6.5
FeO	3.44	4.79	Melilite	4.8
MnO	0.33	0.47	Pyroxene	3.9
MgO	9.22	28.87	Pegowskite	2.0
CaO	34.98	62.38	Pyrite	1.2
BaO	0.08	0.05		100.0
SrO	0.18	0.17		
Na ₂ O	0.05	0.08		
K ₂ O	1.20	1.27		
P ₂ O ₅	3.24	2.35		
S	0.56	1.57		
H ₂ O ^{+110°}	1.02	5.66		
H ₂ O ^{-110°}	0.37			
	100.07			
-O=S	0.21			
	99.88			

Table 1. Spectral analysis of matrix of breccia at Sölskär.

B-b	1	As-b	0	Al-a	2
Cd-b	0	K-c	—	P-b	0
Li-b	—	Fe-a	—	Si-a	2
Co-a	0	Sb-b	0	Sn-a	0
Mn-a	2	Mo-a	1	Zr-c	1
Ta-c	0	Na-b	1	Mg-a	2
Ti-b	2	Zn-b	0	Be-a	0
V-a	1	Tl-b	0	Pb-a	0
Ni-a	0	Nb-c	2	Bi-a	0
Cr-a	0	Ca-b	3	Y	1
Cu-a	1	Ba-c	2	U	0

not yet been analyzed, but their general habit is very similar to pyrochlore and dysanalyte previously collected on the small islands north of Alnö Island. The latter have been analyzed, although the analyses have not yet been published. The chemical and optical data of the present mineral will be given later when the present investigation of the minerals of the Alnö rocks has been completed. The spectral analysis given below confirms the presence of Nb.

A chemical analysis, however, gave 0.031% U and 0.056% Th.

The chemical Analysis No. 2 shows in this case, too, a reversal of the usual Ba/Sr ratio. As the analysis is performed on an average sample the calculated

mode, based on micrometric analyses of 12 thin-slides, does not represent any definite type of rock.

The discovery of the breccia boulders confirms that the consolidation of previously known sövite did not mark the end of volcanic activity. It suggests, however, that it continued on a larger scale than that previously made evident by small carbonatitic dikes intersecting the sövite. These carbonatites generally come from a fairly high level in the volcanic conduit, while all the rocks represented by the breccia must have originated at a far greater depth. This must also be the reason why not a single piece of ouachitite or any garnet is found in the breccia. The alteration of melilite, *inter alia*, to garnet denotes a comparatively late stage of metamorphism and advanced silification.

As no breccia has been found in solid outcrops, the locality from which the boulders originate remains unknown. Probably it has to be looked for somewhere to the north-west under the sea. Perhaps in the very distant future the rising of the land will bring it to the surface.

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Uppsala 1960. Almqvist & Wiksells Boktryckeri AB

Read 25 May 1960

Contributions to the knowledge of the alkaline dikes of the Alnö region I–III

By HARRY VON ECKERMANN

With 10 figures in the text

Introduction

In 1896 A. G. Högbom gave a brief account of the dikes associated with the alkaline and carbonatitic intrusion of the Alnö region. It was his intention to make a more detailed and complete survey of these rocks, but unfortunately he never found time to do so.

When re-investigating the Alnö alkaline intrusion the present author gave special attention to the dikes and in his memoir on "The Alkaline District of Alnö Island" [1] many different types of dikes are mentioned. However, the outcrops are comparatively few and the accessible dike-rocks to a large extent deeply weathered. Mostly the dikes are covered by overburden and inaccessible.

A more comprehensive survey of the dikes was made possible by the blasting, tunnelling and diamond drilling operations carried out in connection with the building of the hydraulic power station at Bergeforsen north-west of the intrusion centre. Thanks to liberal grants from the Swedish State Research Board and the courtesy of the officials of both the Bergeforsen Kraft Aktiebolag and the Royal Swedish State Waterfall Board, (RSSWB), I was given the opportunity of carrying out this survey as well as of publishing the results [2].

A total number of 286 dikes were listed in three series, every dike being given a number ([2], pp. 11–16) and its petrographic character, as deduced from thin-slides. Only 18 were analyzed. Among the remaining 268 are several rock types not represented by previous analyses. Providing that I obtain further financial support, I propose to publish from time to time analyses of selected dike-rocks with appended short mineralogical descriptions. I am hoping that the collocation of these and previous analyses may ultimately lead to a more profound knowledge of the chemical and modal changes of the intrusion during both magmatic and post-magmatic stages, as well as of the secondary rheomorphic magmas derived from liquefied fenites. Light may also be shed on the puzzling and at present unexplainable problem of chemically almost identical dike-rocks occurring with widely different modes.

The petrographic methods and the nomenclature used in the following investigations and descriptions are the same as stated in my Alnö Memoir ([1], pp. 12–16). The modes are determined by checking micrometric analyses of a number of thin-slides against calculated modes until a reasonable agreement is reached. The photographs and microphotographs are all taken by the author.

Analysis No. 1. Kimberlite.

Analyst R. Blix.

	Weight (%)	Mol. prop. × 100	Norm		Mode	%	Niggli's system	
SiO ₂	28.82	47.99	or	14.25	Phlogopitic biotite	33.6	si	+ 50.0
CO ₂	11.31	25.71	ab	4.04	Pseudomorphs of		qz	— 64.0
TiO ₂	1.80	2.25	c	1.53	monticellitic		co ₂	26.61
Al ₂ O ₃	4.92	4.83	Σ sal	19.82	olivine	33.6	ti	2.33
Fe ₂ O ₃	5.36	3.36			Calcite ^a	20.4	al	5.0
FeO	5.69	7.92	di	5.15	Garnet	8.7	fm	53.5
MnO	0.18	0.25	hy	11.53	Apatite	1.8	c	38.0
MgO	14.30	35.47	ol	17.34	Ilmenite	1.4	alk	3.5
CaO	16.76	29.89	mt	7.77	Pyrite	0.5	mg	0.70
BaO	0.14	0.09	il	3.42		100.0	c/fm	0.71
SrO	0.06	0.06	pr	0.47			k	0.77
Na ₂ O	0.48	0.77	ap	1.80			p	0.57
K ₂ O	2.41	2.56	cc	25.93			h	24.93
P ₂ O ₅	0.78	0.55	Σ fem 73.41				w	0.46
S	0.22	0.69					Q	— 1.3
H ₂ O ^{+105°}	4.34	24.09					L	16.1
H ₂ O ^{−105°}	2.35	—	H ₂ O	6.69			M	85.2
	99.92			99.92			π	0.18
—O—S	0.11						γ	4.05
	99.81						α	0.42
							μ	0.41

Quantitative system: IV : 2 : 3 : 1 : 2. Or: ab: an: — 78: 22: 0. Sp. gravity $\frac{20}{4}$ C°: 2.762.^a Total calcite 26.4%, thereof about 6 % in the pseudomorphs of olivine.

The first three instalments of the series follow below. I have to thank the Swedish State Research Board for supporting grants and the Aktiebolaget Atomenergi (Atomic Energy Co. Ltd.) for spectral and chemical analyses.

I. Kimberlite dike from the right-hand inspection tunnel at Bergeforsen

The sample was taken from the lower branch of dike No. 26, Table 2 ([2], p. 14), corresponding to dike No. 19 in drawing No. 706719-6209 of the RSSWB.

The projection point in Niggli's QLM-diagram falls to the left of and slightly outside the area previously established for alnöites, kimberlites and ouachitites (cf. [2], p. 25, Fig. 12). The rock contained originally a fair amount of melilite, later autometamorphically altered into garnet, carbonate and a residue of mica mixed with clay minerals, probably of illitic and montmorillonitic compositions. Chemically, the rock occupies an intermediary position between kimberlites and olivine-melilitites (cf. [2], p. 42, Analysis XII).

The texture of the rock is porphyritic with large pseudomorphs of monticellitic olivine in a medium grained ground-mass. The flow orientation of the latter is marked by the mica and the melilite-pseudomorphs (Figs. 1 and 3).

The pseudomorphs of olivine are of varying size: from 1–4 mm long and up to 3 mm wide. Their original crystal boundaries are well preserved. Occasionally unaltered olivine kernels are still preserved (Fig. 2), but mostly the crystals are totally altered

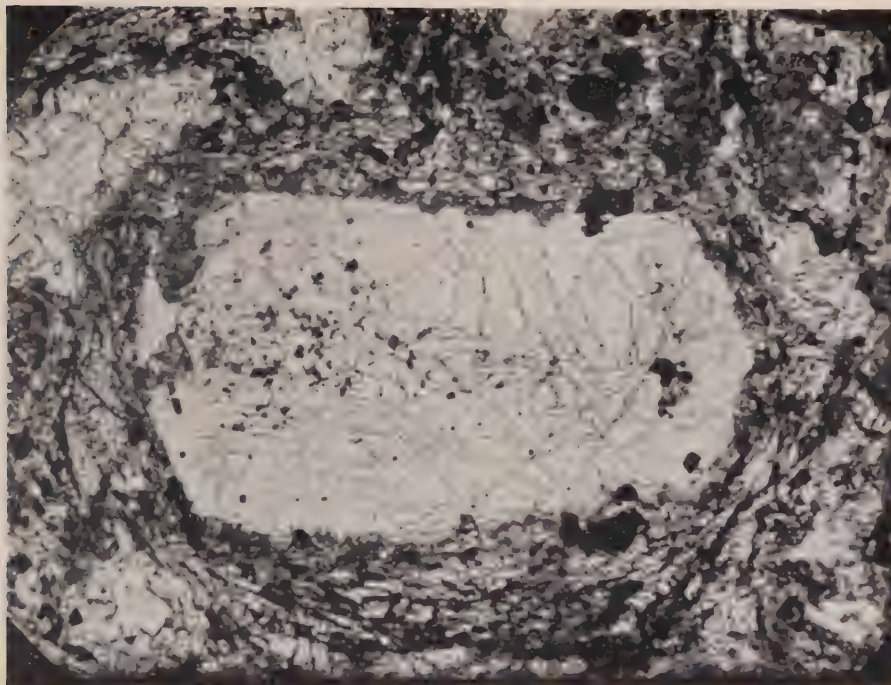


Fig. 1. Serpentinized olivine crystal in a ground-mass of phlogopitic mica, melilite pseudomorphs and calcite. The black minerals are pyrites and ilmenite (pseudomorphs of perowskite). Ordinary light. $\times 40$.

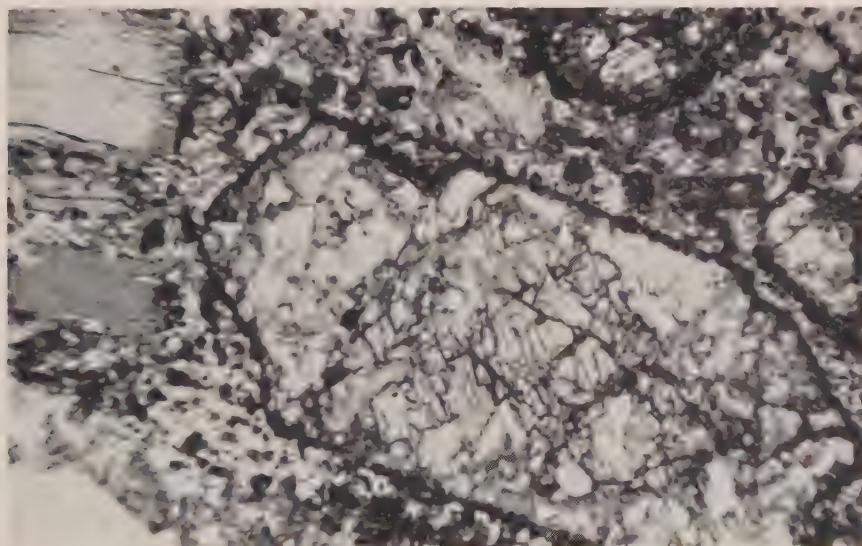


Fig. 2. Olivine phenocryst with unaltered kernel (darker grey) and serpentinized marginal zones. A narrow fringe of small grains of iron ore (black) designates the crystal boundary. To the left, two phlogopitic biotites, the upper one with a chloritic margin (darker grey). Ordinary light. $\times 40$.

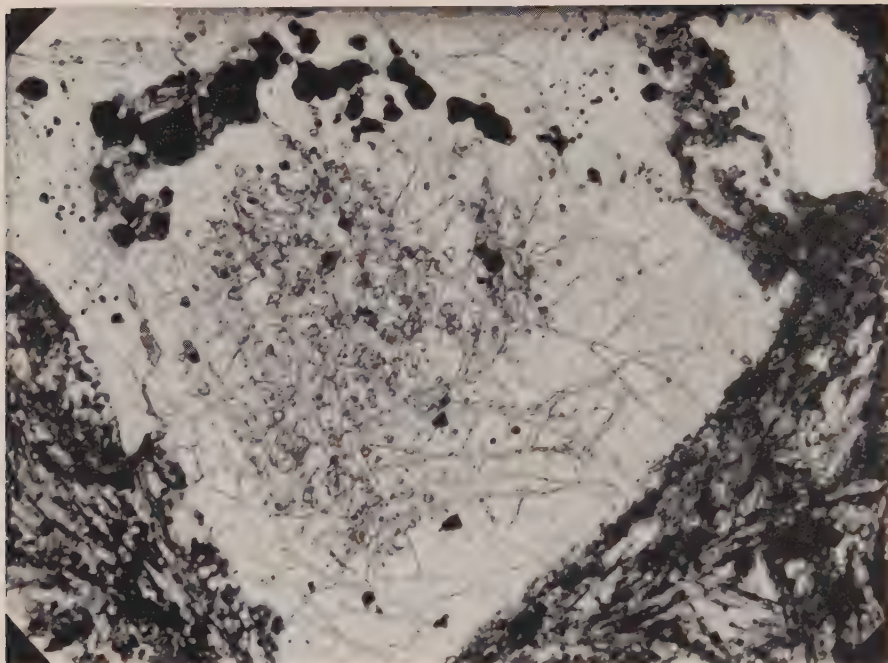


Fig. 3. Olivine pseudomorph with calcite grains in light green serpentine indicating a primarily monticellitic kernel at one end of the crystal, while the remaining part shows large and small magnetite crystals in a green serpentine. The zonal growth of the original crystal has in this case not been concentric, and the marginal growth hyalosideritic. Ordinary light. $\times 40$.



Fig. 4. Calcite grains in the kernel of a monticellitic olivine pseudomorph. The black grains are magnetite. Ordinary light. $\times 60$.

Analysis No. 2. Ouachitite.

Analyst R. Blix.

Weight (%)	Mol. prop. × 100	Norm	Mode	%	Niggli's system
SiO ₂	17.93	29.85	or 5.34	Carbonate	si + 30.5
CO ₂	15.04	34.18	ab 0.94	(cc ₈₂ mgt ₁₈) ^a	qz - 73.5
TiO ₂	1.84	2.30	c 8.31	Biotite and	co ₂ 34.96
Al ₂ O ₃	9.47	9.29	Σ sal 14.59	chlorite	ti 2.95
Fe ₂ O ₃	4.11	2.57		Garnet	al 9.5
FeO	6.61	9.20		Olivine -	fm 39.0
MnO	0.27	0.38	di 8.77	pseudomorphs	c 50.0
MgO	9.67	23.98	hy 5.88	Apatite	alk 1.0
CaO	24.00	42.80	ol 14.35	Magnetite	mg 0.62
BaO	0.16	0.10	mt 5.96	Ilmenite	c/fm 1.29
SrO	0.12	0.12	il 3.49	Pyrite	k 0.84
Na ₂ O	0.11	0.18	pr 0.17		p 1.51
K ₂ O	0.90	0.96	ap 4.83		h 34.84
P ₂ O ₅	2.10	1.48	cc 34.37		w 0.36
S	0.08	0.25	Σ fem 77.82		Q - 7.2
H ₂ O ^{+105°}	5.37	29.81			L 18.9
H ₂ O ^{105°}	2.12	—	H ₂ O 7.49		M 88.3
	99.90		99.90		π 0.81
-O=S	0.04				γ 0.52
	99.86				α - 0.81
					μ 0.30

Quantitative system: IV : 2 : 3 : 1 : 2. Or: ab: an: 85: 15: 0. Sp. gravity $\frac{20}{4}$ C°: 3.066.

^a Average composition.

into a greenish serpentine with a usually centrally located poikilitic intergrowth of serpentine and calcite (Figs. 3 and 4). Occasionally, in small pseudomorphs calcite grains occur in decreasing frequency from the centre to the crystal boundaries. In consequence, the primary olivine has been of zonal growth with monticellitic kernels and forsteritic rims. A few pseudomorphs contain no calcite and indicate an originally later generation of forsterite.

The mica is of a light brown colour with dark brown pleochroism. Its low refraction, = 1.571, and its high magnesia content calculated from the mode indicate a phlogopitic composition. The mica is surrounded by chloritic rims and reaches 0.5 mm in length.

The calcite occurs partly within the melilite, perovskite and monticellite pseudomorphs and partly interstitially in the ground-mass. The garnet is occasionally crystallized as small yellow crystals of 0.2–0.3 mm in diameter with purplish brown kernels of melanite, but occurs mostly as grainy aggregates within the melilite pseudomorphs.

The apatite seems to have been the first crystallized mineral and occurs as 0.2–1.0 mm long prisms. Ilmenite is only observed as pseudomorphs of perovskite. Although not shown in the mode, fluorite is occasionally found in the interstices. Nicely crystallized minute pyrites also belong to the last crystallization products.



Fig. 5. Flow-texture of ouachititic dike rock, running diagonally across the photograph, and designated by the biotite (light grey and white) and some of the melilite pseudomorphs (dark grey and black). Two black angular patches to the right and left in the upper part of the picture are melanite crystals. The irregular white patches to the upper right are calcite. Ordinary light. $\times 60$.

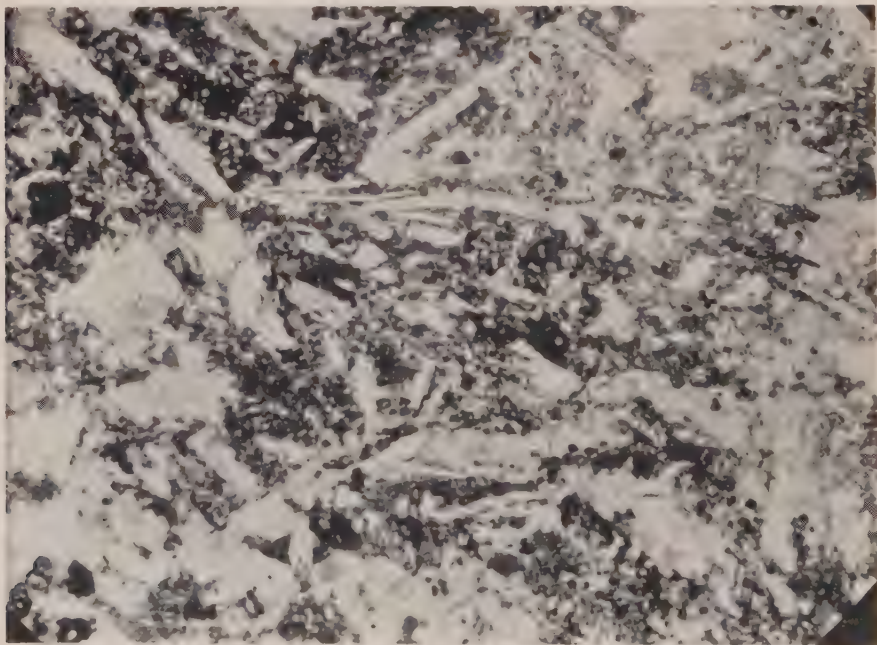


Fig. 6. Dark grey spotted areas are grainy aggregates of yellow garnet from individually not discernable melilite pseudomorphs. To the upper left yellow garnets with melanitic kernel (black). Ordinary light. $\times 40$.



Fig. 7. Triangular interstitial area in ouachititic dike-rock framed by biotite. Biotite crystals also cut across the lower left corner and protrude from the right side of the triangle, which latter is filled by calcite. At the lower right corner a serpentinized olivine pseudomorph. The dark grey areas are yellow garnet and the black either melanite or magnetite. A couple of small black spots within the triangle are pyrites. Ordinary light. $\times 60$.

II. Ouachititic dike from the right-hand inspection tunnel at Bergeforsen

The sample was taken from the middle branch of dike No. 28, Table 2 ([2], p. 14), corresponding to the lower branch of dike No. 22 in drawing No. 706719–6209 of the RSSWB.

The projection point in Niggli's QLM-diagram falls just outside the lower left corner of the previously established area of alnöites (kimberlites) and ouachitites ([2], p. 25, Fig. 12). Probably the rock originally contained a large percentage of melilite, but pseudomorphs are only occasionally discernible owing to recrystallization.

The original flow-texture is still recognizable here and there (Fig. 5) by the orientation of melilite pseudomorphs and mica, but generally the garnet of the individual pseudomorphs has merged into large areas of small garnet crystals or recrystallized into fairly big crystals.

The carbonate occurs partly in the pseudomorphs of melilite, where its refraction indicates a dolomitic composition, partly in the pseudomorphs of perowskite and partly as calcite in larger aggregates and in the interstices of the texture.

The mica is of a dirty yellowish colour with green chloritic margins. It is a biotite with a fairly high magnesia content. The size seldom exceeds 0.5 mm in length, but occasionally reaches $1\frac{1}{2}$ mm.



Fig. 8. Ouachitite. In the upper centre a mica crystal with dark chloritic margins. The white-spotted dark areas are grainy aggregates of garnet. A couple of larger yellow garnet crystals are seen about 1 cm below the left end of the above-mentioned mica. The light grey and white areas are carbonate. Ordinary light. $\times 60$.

The garnet occurs partly as irregular aggregates of very small grains and partly as well shaped crystals of up to 0.5 mm diameter with melanitic purplish-brown kernels. While the kernels are isotropic the yellow rims are slightly birefringent.

Olivine pseudomorphs occur here and there. They are small, 0.2–0.4 mm, composed of serpentine only and of a greenish white colour, indicating an originally forsteritic composition. Occasionally fluorite is found in the interstices of the texture.

Apatite crystals of up to 1 mm in length, numerous small grains of magnetite, some small pyrite crystals and ilmenite pseudomorphs of perovskite make up the accessories.

III. Radioactive beforsitic carbonatite dike

At the junction of the main road No. 13 and the local road to Fagervik, about 300 m SSW of the power station at Bergeforsen, both roads cut through a rocky hillock. At the left corner of the junction, facing Fagervik, an almost vertical, about half a meter broad Alnö dike intersects the local gneiss granite in a southeasterly direction, at the same time cutting through a porphyritic jotnian dike at an oblique angle. The dike is easily recognized by its reddish-brown weathering and by its radioactivity. It continues at deeper levels, crossing the Fagervik water tunnel

Analysis No. 3. Partly weathered beforosite, rich in barite.

Analyst R. Blix.

	Weight (%)	Mol. prop. × 100	Mode	%	Niggli's system	
SiO ₂	30.07	50.07	Carbonate		si	94.0
CO ₂	12.14	27.59	(cc ₅₂ mgt ₃₅ sdt ₉ rdt ₄)	24.6	qz	— 34.0
TiO ₂	2.28	2.85	Soda-orthoclase		co ₂	48.76
Al ₂ O ₃	6.27	6.15	(or ₉₅ ab ₅)	19.7	ti	4.26
Cr ₂ O ₃	0.07	0.05	Goethite	15.2	al	11.5
Fe ₂ O ₃	13.33	8.35	Barite	13.1	frn	55.0
FeO	1.25	1.74	Quartz	12.4	c	26.5
MnO	0.66	0.93	Clay minerals	9.8	alk	7.0
MgO	4.03	10.00	Rutile	2.4	mg	0.34
CaO	7.90	14.09	Apatite	1.2	c/frn	0.43
BaO	8.40	5.48	CO ₂	1.1	k	0.95
SrO	0.15	0.15	Fluorite	0.5	p	0.97
Na ₂ O	0.11	0.18		100.0	h	29.06
K ₂ O	3.32	3.52			w	0.91
P ₂ O ₅	0.52	0.37			Q	19.5
ThO ₂	0.05	0.02			L	26.0
UO ₃	0.04	0.01			M	54.5
F	0.19	1.00			π	0.24
SO ₃	4.40	5.50			γ	0.29
H ₂ O ^{+105°}	2.80	15.54			α	0.12
H ₂ O ^{-105°}	2.01	—			μ	0.24
	99.99					
-O F	0.08					
	99.91					

split up into three branches, numbered 24, 25 and 26 in my previous paper on the dikes ([2], Table 1 and Plate XIX).

The weathering of the dike has a depth of several meters. While in the tunnel the dike is a typical white beforosite with dolomitic carbonate and occasional crystals of phlogopitic mica, the slightly weathered dike is greenish, due to chloritization of the mica, and the strongly weathered brown. Two analyses were made, one of the rock, which although weathered still keeps together, and one of the crumbled reddish brown residue (analyses No. 3 and 4).

The carbonate is partly an ankeritic dolomite and partly calcite. While the former occasionally is nicely crystallized, the latter fills the interstices together with quartz and clay minerals. The composition of the carbonate as given in the mode, indicates an average of both carbonates. The dolomitic one contains numerous small vesicles visible at high magnification, which contain carbonic acid. Probably, the total content of free CO₂ given in the mode is higher than 1.1 %, as some must have been released when crushing the sample in preparation for analysis. Carbonatitic dikes with free CO₂ have previously been discovered (cf. [1], pp. 118, 120–122), but never with such a high silica and barium content.

The soda-orthoclase occurs partly as badly crystallized phenocrysts and partly in the interstices. Twinning is very rare. The barite, on the other hand, is generally nicely crystallized with well-defined boundaries, the crystals being evenly scattered throughout the rock.

Analysis No. 4. Fully weathered and decomposed beforosite.

Analyst R. Blix.

	Weight (%)	Mol. prop. × 100	Mode	%	Niggli's system	
SiO ₂	28.30	47.12	Goethite	21.2	si	109.0
CO ₂	8.22	18.68	(Soda) Orthoclase		qz	-17.0
TiO ₂	2.93	3.67	(or ₉₇ ab ₃)	16.9	co ₂	43.03
Al ₂ O ₃	7.30	7.16	Barite	16.3	ti	8.46
Cr ₂ O ₃	0.06	0.04	Carbonate		al	16.5
Fe ₂ O ₃	18.46	11.56	(ce ₄₅ mg _{t41} sdt ₁ rdt ₁₀)	14.8	fm	58.5
FeO	0.35	0.49	Quartz	13.0	c	18.5
MnO	0.90	1.27	Clay minerals	11.4	alk	6.5
MgO	2.82	6.99	Rutile	3.1	mg	0.22
CaO	4.57	8.15	CO ₂	1.6	c/fm	0.32
BaO	10.42	6.80	Apatite	1.1	k	0.92
SrO	0.02	0.02	Fluorite	0.6	p	0.74
Na ₂ O	0.05	0.08		100.0	h	49.00
K ₂ O	2.72	2.89			w	0.98
P ₂ O ₅	0.45	0.32			Q	27.0
ThO ₂	0.27	0.10			L	29.5
UO ₃	0.05	0.02			M	43.5
F	0.24	1.26			π	0.44
SO ₃	5.50	6.87			γ	0.13
H ₂ O ^{+105°}	3.83	21.26			α	0.52
H ₂ O ^{-105°}	2.67				μ	0.19
	100.13					
-O=F	0.10					
	100.03					

The clay minerals are isotropic or almost so, and their composition could not be determined microscopically. The goethite also occupies an interstitial position or represents pseudomorphs of earlier minerals, probably mostly micas. The apatite is present as long narrow prisms.

The most interesting of the minerals is the rutile. Anatase has previously been observed in Alnö carbonatites, the first time by A. G. Högbom, who labelled it "an unknown blue mineral", and later by the present author (cf. [1], pp. 106, 107, 118 and 130). The rutile occurs fairly evenly distributed within the rock. On account of its high refraction it appears almost black in the thin-slides and only in a few larger crystals is its greenish-yellow colour visible. It is occasionally surrounded by yellow reaction rims in the carbonate and the rutile seems to be responsible for the radioactivity of the rock. Generally the radioactivity of the Alnö rocks depends upon the presence of minerals of the perovskite-dysanallyte-pyroxhlore series, but no such minerals are found in the present carbonatite.

A few minute crystals of high refraction, but lower than that of rutile, may be zircon. No reaction rims due to radioactivity have, however, been observed.

The Aktiebolaget Atomenergi performed two spectral analyses on two different samples, collected by me at different times. They show that the strongly weathered rock is not quite homogeneous, the difference possibly being due to a locally uneven rate of weathering. The analyses are given above, the first figure referring to the first and the second to the second sample.



Fig. 9. The barium-bearing carbonatite. Black areas indicate mostly goethite, to the upper right, pigmenting a mica pseudomorph. About $1\frac{1}{2}$ cm to the left of the lower end of the latter a small apatite. To the middle left about 1 cm from the margin, a rutile "needle". The dark grey areas are mostly barite and some dolomite, the light grey ones dolomite and the white ones orthoclase, calcite, quartz and clay minerals. Ordinary light. $\times 25$.

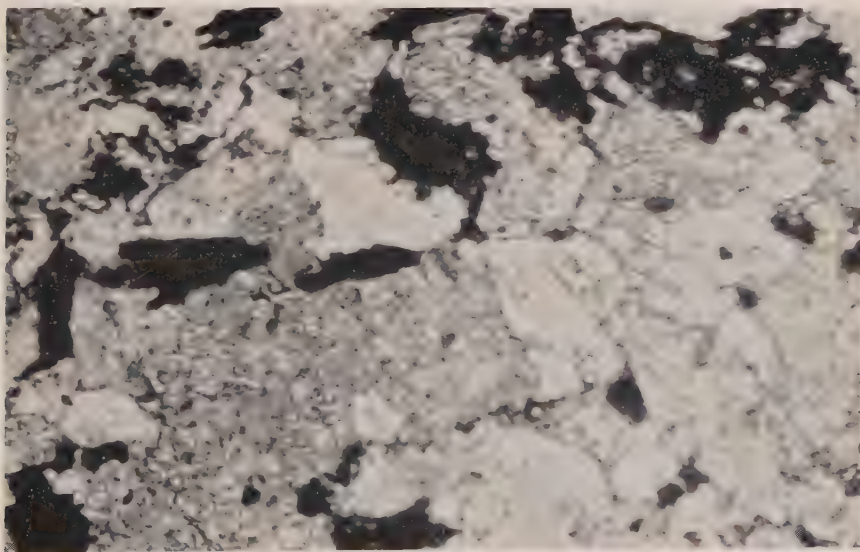


Fig. 10. Carbonatite. Black areas are goethite and rutile (two small crystals at the lower right). To the lower left a barite crystal of rectangular shape. At its right end and above it soda-orthoclase (white). The remaining light and dark grey grains are carbonate. Ordinary light. $\times 60$.

Table 1.

B-b	0-0	As-b	0-0	Al-a	2-2
Cd-b	0-0	K-c	—	P-b	0-0
Li-b	—	Fe-a	3-	Si-a	3-2
Co-a	0-0	Sb-b	0-0	Sn-a	0-0
Mn-a	1-2	Mo-a	0-1	Zr-c	1-1
Ta-c	0-0	Na-b	1-1	Mg-a	2-3
Ti-b	2-2	Zn-b	0-0	Be-a	0-0
V-a	1-1	Tl-b	0-0	Pb-a	0-1
Ni-a	1-1	Nb-c	0-1	Bi-a	0-0
Cr-a	1-2	Ca-b	2-2	Y	1-2
Cu-a	1-2	Ba-c	2-2	U	0-0

A chemical analysis gave, however, 0.033 % U. It was not possible to determine microscopically in which minerals the Y, V, Ni and Cr enter. As to the Cu, occasional very small crystals occur within the goethite, which could be chalcopyrite. The Nb is previously known to occur in rutile. As no pyrochlor crystals have been found in the thin-slides this is probably the case in this instance, too.

The fully weathered beforite contains the same components as the partly weathered, the main difference being the removal of some of the orthoclase and carbonate and a corresponding concentration of the goethite, barite, clay minerals, quartz and rutile. The increased percentage of rutile is accompanied by an increase in radioactivity. Measured with a "Hoffman scaler" against a background of 40 counts/min, I obtained a gradual variation from 201 counts/min to 320 counts/min when moving the GM-counter from the partly weathered part of the dike to the fully weathered. A later check on an average sample, made by the prospecting department of Aktie bolaget Atomenergi, gave 249 counts/min against a background of 37 counts/min. An analysis of the thorium content gave a lower value than that obtained by Blix in analysis Nr. 4, viz. 0.043 % Th.

The increase in carbonic acid from 1.1 to 1.6 % may be due to an incidentally higher percentage in this sample, but it is more likely that less grinding of the sample when preparing it for analysis is responsible, owing to the consequent smaller escape of the gas.

Compared with previously known dikes this one is unique. Such a high barite content has not before been observed in any conesheet dike. The presence of rutile is also a departure from previously known mineral parageneses.

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Orthopinakiolite, a new modification of $\text{Mg}_3\text{Mn}^{2+}\text{Mn}_2^{3+}\text{B}_2\text{O}_{10}$ from Långban, Sweden

By REIN RANDMETS

ABSTRACT

Orthopinakiolite, $\text{Mg}_3\text{Mn}^{2+}\text{Mn}_2^{3+}\text{B}_2\text{O}_{10}$, is an orthorhombic modification of pinakiolite. The unit cell lengths are $a = 18.45 \pm 0.3$ Å, $b = 12.70 \pm 0.2$ Å, $c = 6.07 \pm 0.1$ Å and the probable space groups $Pnn2$ or $Pnnm$. The unit cell contains 8 formula units. The density is 4.03 g/cm³. The mineral occurs as black needles in dolomite together with hausmannite. Orthopinakiolite is much rarer than the monoclinic pinakiolite but the mode of occurrence is the same. The four strongest lines in the powder pattern of orthopinakiolite are: 5.17 Å (9); 2.59 Å (10); 2.52 Å (9); 2.03 Å (9) (Fe-radiation).

Introduction and previous investigations

Pinakiolite is a very rare mineral and as to this writer's knowledge it has been found only in the Långban mine. The mineral was named by Flink (1890) who described it as orthorhombic. Bäckström (1895) investigated another mineral from Långban, the chemical composition of which was the same as that of pinakiolite. Bäckström found also that the physical properties such as hardness and specific gravity were in good agreement with each other.

As for the morphology and crystallographic constants the two minerals differed. Whereas pinakiolite formed small thin tablets after the (100) pinacoid and showed a characteristic twinning {011}, the other mineral appeared as acicular crystals, lacking pinacoids and twinning. The axial ratio for pinakiolite determined by Flink was $a:b:c = 0.83385:1:0.58807$ and the axial ratio for the new mineral according to Bäckström $a:b:c = 0.6828:1:?$.

Bäckström concluded that the new mineral was probably orthorhombic like pinakiolite, but that they were different species. Being able to measure the mineral in one zone only, owing to lack of pyramidal faces, he did not give the mineral a new name.

In 1949 Takéuchi, Watanabé and Ito determined the crystal structures of warwickite, ludwigite and pinakiolite, all three being boron-bearing minerals and closely related structurally. According to these writers the pinakiolite crystal used in their investigation was a thin plate. They found the unit cell to be monoclinic and the space group $C_{2h}^2-P2_1/m$. The dimensions of the unit cell were $a = 5.36 \pm 0.05$ Å; $b = 5.98 \pm 0.02$ Å; $c = 12.73 \pm 0.04$ Å; $\beta = 120^\circ 34'$.

The purpose of the present investigation is: (1) to determine the unit cell and the space group of the pinakiolite-related mineral, first investigated by Bäckström and in the following called orthopinakiolite; and (2) to find out if there are still other modifications of pinakiolite.

Material, occurrence and paragenesis

At the writer's disposal was the whole pinakiolite collection of the Mineralogical Department of the Swedish Museum of Natural History, consisting of about 150 hand specimens. Powder photographs were taken of all specimens. From these photographs twelve were identified as orthopinakiolite and the rest as pinakiolite. No other modifications were found.

According to Bäckström the orthopinakiolite occurs in granular dolomite in vein-like fields together with hausmannite, manganophyllite and sometimes pinakiolite. In the present material orthopinakiolite was not found together with pinakiolite, but otherwise the occurrence is the same.

Aminoff (1918), in a paper on the paragenesis of the Långban minerals, supposed the pinakiolite to belong to the same period of mineral formation as the berzeliite-hedyphane association and the skarn minerals.

Magnusson (1930) has given a paragenetic classification of the minerals in the Långban deposits. He divided the mineral-forming process into three periods. The temperature was low at the beginning, increased to a maximum (thermometamorphism) in the middle of the second period and then sank again. According to him pinakiolite was formed during the first part of the third period, being distinctly younger than hausmannite.

As mentioned above, orthopinakiolite and pinakiolite do not occur together, but as they both are followed by the same minerals, it is suggested that the two minerals belong to about the same period of mineral formation.

Unit cell and space group

A very thin acicular crystal of orthopinakiolite was chosen for the rotation and equi-inclination photographs (zero and first layer lines) around the needle-axis (*c*-axis). Ni-filtered Cu-radiation ($\text{CuK} = 1.5418 \text{ \AA}$) was used. The unit cell was found to be orthorhombic within the limits of error with following dimensions: $a = 18.45 \pm 0.3 \text{ \AA}$; $b = 12.70 \pm 0.2 \text{ \AA}$; $c = 6.07 \pm 0.1 \text{ \AA}$; which yielded the axial ratio $a:b:c = 1.453:1:0.478$. By transformation (changing the *a*- and *b*-axes) a new ratio, $a:b:c = 0.696:1:0.329$, is obtained which agrees approximately with the one found by Bäckström. There are eight molecules of $\text{Mg}_3\text{Mn}^{2+}\text{Mn}_2^{3+}\text{B}_2\text{O}_{10}$ in the unit cell.

The reflections observed in the Weissenberg photographs satisfy the following conditions:

$(h00)$	$h = 2n$	$(h01)$	$h = 2n + 1$
$(0k0)$	$k = 2n$	$(0k1)$	$k = 2n + 1$
$(hk0)$	no conditions	$(hk1)$	no conditions

From these observations the following general conditions can be concluded:

$$\begin{aligned}(0kl) \quad k + l &= 2n \\ (h0l) \quad h + l &= 2n\end{aligned}$$

Table 1. X-ray powder data of orthopinakiolite and pinakiolite ($\text{FeK}_\alpha = 1.9373 \text{ \AA}$ Mn-filter).

Orthopinakiolite				Pinakiolite			
<i>I</i>	<i>d</i> (meas.)	<i>hkl</i>	<i>d</i> (calc.)	<i>I</i>	<i>d</i> (meas.)	<i>hkl</i>	<i>d</i> (calc.)
2	5.90	101	5.76	8	5.39	101	5.35
9	5.17	111	5.25	2	4.94	102	5.00
2	3.52	411	3.53	2	3.61	{ 003	3.66
7	3.01	{ 002	3.03	4	3.00	{ $\bar{1}$ 01	3.66
		{ 331	3.02			{ 020	2.99
		{ 610	3.00			{ $\bar{1}$ 02	2.89
6	2.79	{ 521	2.82	10	2.70	{ 210	2.76
		{ 212	2.81			{ 004	2.75
		{ 141	2.78	8	2.50	{ 105	2.55
10	2.59	{ 710	2.58			{ 201	2.54
		{ 341	2.56			{ $\bar{1}$ 03	2.35
9	2.52	{ 531	2.53	3	2.31	{ 115	2.34
		{ 621	2.52			{ 211	2.34
		{ 150	2.52			{ $\bar{1}$ 21	2.32
4	2.49	412	2.49	2	2.24	{ 200	2.31
3	2.37	{ 701	2.42			{ 214	2.30
		{ 711	2.37			{ 016	2.27
3	2.29	{ 151	2.32	7	2.16	{ 005	2.20
		{ 800	2.31			{ $\bar{1}$ 13	2.19
		{ 512	2.30			{ 124	2.17
8	2.20	{ 631	2.30	3	2.07	{ $\bar{1}$ 22	2.12
		{ 251	2.27			{ 201	2.06
		{ 721	2.26	7	1.990	{ 031	1.975
1	2.12	{ 351	2.19			{ $\bar{1}$ 04	1.965
		{ 142	2.18			{ 310	1.957
		{ 612	2.13	3	1.837	{ $\bar{2}$ 11	1.950
1	2.08	{ 811	2.13			{ 132	1.886
		{ 910	2.12			{ 131	1.868
9	2.03	{ 060	2.11	2	1.807	{ 006	1.831
		{ 160	2.10			{ 107	1.786
		{ 731	2.10	6	1.631	{ 301	1.646
7	1.916	{ 821	2.04			{ $\bar{1}$ 24	1.643
		{ 103	2.01			{ $\bar{1}$ 32	1.641
		{ 911	1.920	4	1.548	{ 108	1.547
4	1.763	{ 123	1.916			{ 300	1.542
		{ 931	1.765			{ 127	1.534
2	1.675	{ 912	1.684	6	1.520	{ 218	1.530
		{ 613	1.675			{ $\bar{1}$ 33	1.521
		{ 371	1.673	4	1.504	{ 410	1.504
1	1.659	{ 135	1.640			{ 141	1.440
		{ 080	1.587			{ 231	1.434
5	1.579	{ 180	1.582	2	1.433	{ 142	1.432
		{ 153	1.576			{ 0.1.10	1.432
		{ 172	1.552				
8	1.523	{ 281	1.538				
		{ 12.0.0	1.537				
		{ 181	1.531				
4	1.512	{ 004	1.517				
		{ 114	1.501				
		{ 214	1.486				
3	1.468	{ 124	1.470				
		{ 314	1.463				
		{ 163	1.458				
4	1.376	{ 134	1.423				
		{ 091	1.375				
		{ 191	1.371				
6	1.307	14.0.0	1.317				

Table 2.

	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
<i>Orthorhombic group</i>				
Warwickite	$D_{2h}^{16}\text{-Pnam}$ (Mg, Fe) ₃ Ti[O ₃ BO ₃] ₂	9.20	9.45	3.01
Ludwigite	$D_{2h}^9\text{-Pcma}$ (Mg, Fe ²⁺) ₂ Fe ³⁺ [O ₂ BO ₃]	9.14	12.45	3.05
Paigeite	$D_{2h}^9\text{-Pcma}$ (Fe ²⁺ , Mg) ₂ Fe ³⁺ [O ₂ BO ₃]	9.37	12.36	3.05
Orthopinakiolite	$C_{2v}^{10}\text{-Pnn2}$ or $D_{2h}^{12}\text{-Pnnm}$ (Mg, Mn ²⁺) ₂ Mn ³⁺ [O ₂ BO ₃]	2 × 9.23	12.70	2 × 3.04
<i>Monoclinic group</i>				
Pinakiolite	$C_{2h}^2\text{-P2}_1/m$ (Mg, Mn ²⁺) ₂ Mn ³⁺ [O ₂ BO ₃]	5.36	5.98	12.73
			$\beta = 120^\circ 34'$	

Thus the space group is determined to be either $C_{2v}^{10}\text{-Pnn2}$ or $D_{2h}^{12}\text{-Pnnm}$ (Nos. 34 and 58 in the International Tables).

The specific gravity of orthopinakiolite determined by Bäckström, by weighing his mineral specimen in benzene, was 3.935. Using the same method the present writer found the density of orthopinakiolite to be 4.03 ± 0.05 g/cm³.

Choice of name

The prefixes *pseudo*, *para*, *meta*, *ortho*, etc. seem to be used without consistency in the mineralogical nomenclature when a new mineral modification is to be named. For example let us look at the prefix *para*:

celsian monoclinic and *paracelsian* pseudo-orthorhombic (Spencer, 1942);

wollastonite triclinic and *parawollastonite* monoclinic (Peacock, 1935);

hilgardite monoclinic and *parahilgardite* triclinic (Hurlbut, 1938), and so forth.

However, there seems to be greater consistency as for the prefixes *clino* and *ortho*. Usually *clino* is used in connection with monoclinic, and *ortho* in connection with orthorhombic modifications of the same mineral. In the present investigation pinakiolite being monoclinic and the new mineral being orthorhombic, the author has used the new name *orthopinakiolite* in analogy with orthoferrosilite (Henry, 1935), orthoguarinite (Cesàro, 1932).

The powder pattern

The X-ray powder data of pinakiolite and orthopinakiolite is presented in Table 1. For these photographs Mn-filtered Fe-radiation was used (FeK = 1.9373 Å). Camera diameter was 114.83 mm. The intensities and *d*-values show the difference as well as the similarity between the two minerals. The four strongest lines of orthopinakiolite are: 5.17 Å (9); 2.59 Å 10); 2.52 Å (9); 2.03 Å (9).

Comparison between the warwickite-ludwigite group and orthopinakiolite

Orthopinakiolite is a natural member of the warwickite-ludwigite group. The empirical chemical formula of this mineral is analogous to that of ludwigite, except that iron in ludwigite is replaced by manganese in orthopinakiolite. As for the unit cell the a and c unit cell lengths of orthopinakiolite are approximately double the a and c values of ludwigite, whereas the b axes are almost equal. This is seen in Table 2.

The volume of one unit cell of orthopinakiolite is four times the volume of the unit cell of ludwigite, depending on the doubling of the a - and c -axes of orthopinakiolite.

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Uppsala 1960. Almqvist & Wiksells Boktryckeri AB

Zur Frage der pneumatolytischen Vorgänge

Von J. ARVID HEDVALL

Mit 14 Abbildungen im Text

Der Begriff Pneumatolyse und die Einwirkungsart solcher Prozesse bei der Bildung von Mineralien und ihre kristallographische Einwirkung bietet immer noch viele ungelöste oder unvollständig behandelte Probleme dar.

Die diesbezüglichen Prozesse können in drei Hauptgruppen geteilt werden nämlich: (a) die direkt chemischen Reaktionen, wobei z.B. Sulfide, Fluoride durch Umsetzungen von festen Substanzen mit anwesenden Erdgasen entstehen; (b) die Einwirkung auf chemische oder kristallographische Prozesse von durch solche Reaktionen gebildeten Schmelzen, die als *agents minéralisateurs* eine Rolle spielen und (c) die Einwirkung von chemisch nicht im gewöhnlichen Sinne reagierenden Gasen auf das Phasengrenzpotential Feststoff-Gas, so dass dadurch der Zuwachs gewisser Oberflächen gefördert und dadurch die kristallographisch besonders wohl — und in vielen Fällen charakteristisch — entwickelten Kristalle entstehen.

In diesem Aufsatz sollen einige Ergebnisse, die für die letztere Gruppe (c) ein Interesse besitzen und im solchen Zusammenhang vorher kaum beachtet wurden, kurz beschrieben werden.

Im Prinzip wird vorerst hervorgehoben, dass wir — trotz aller grundlegend wichtiger Untersuchungen z. B. von de Boer, Langmuir, Stranski und Volmer — immer noch viel zu wenig wissen von den Vorgängen an Oberflächen der festen Körper, namentlich hinsichtlich Veränderungen der spezifischen Oberflächenstruktur bei Temperaturänderungen oder durch Einwirkung von umgebenden im gewöhnlichen Sinne chemisch nicht angreifenden Gasen, z. B. von Sauerstoff oder Stickstoff auf Oxyde bei solchen Temperaturen, wo chemische Reaktionen nicht in Frage kommen können.

Zuerst sollen die von Cohen dilatometrisch festgestellten und von uns¹ weiter untersuchten Strukturumwandlungen in Oberflächenschichten genannt werden. Bei Temperaturen, wo für die betreffenden Stoffe keine Strukturänderungen *ihrer Gitter* existieren, treten umwandlungsähnliche Prozesse in den Oberflächenschichten auf, die sich auch durch Änderungen ihrer chemischen Eigenschaften bemerkbar machen (vgl. Abb. 1 u. 2). Vorläufig sind solche Effekte nur für einige Metalle (Cu, Bi, Sb) festgestellt¹. Zweifelsohne kommen auch andere Metalle in Frage und eventuell auch nichtmetallische Stoffe. Solche Untersuchungen sind vorbereitet.

Hier liegt also noch ein Beispiel vor von der allgemein gültigen Regel, dass jede Substanz, die sich in irgend einem Umwandlungszustande befindet, ein rela-

¹ Vgl. J. A. Hedvall, „Reaktionsfähigkeit fester Stoffe“, S. 136 (A. Barth, Leipzig 1938.)

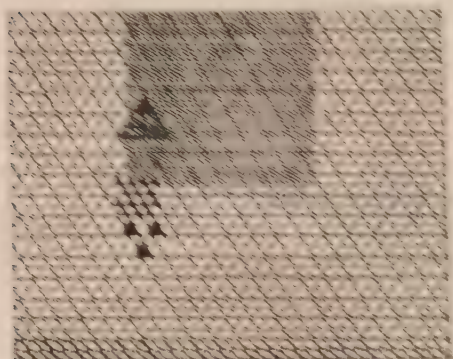


Abb. 1. Mosaikstruktur von ZnO nach Debye.

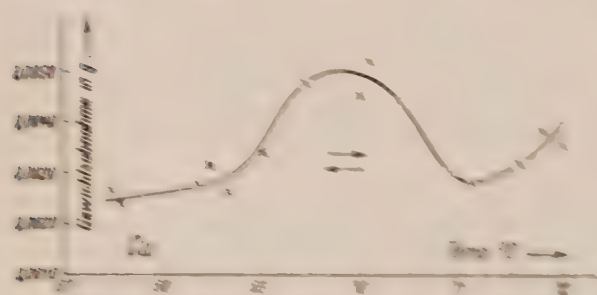
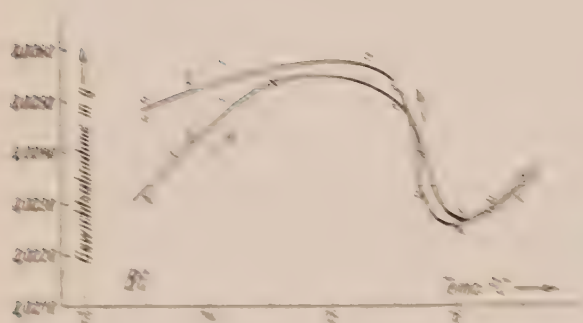


Abb. 2.

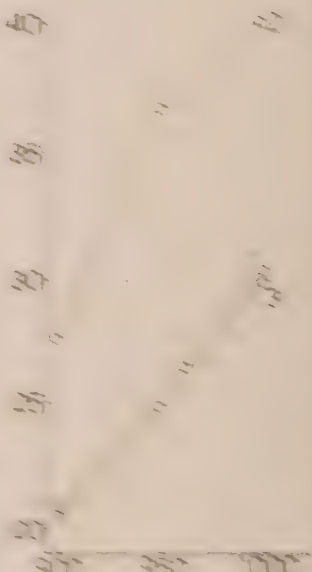


Abb. 3.

Abb. 2. Das Maximum der Änderungen der Oberflächenspannung in den 12 Stunden bei ZnO und ZnO .

Abb. 3. Die Änderungen der Oberflächenspannung in den 12 Stunden bei ZnO und ZnO auf der Ordinate. Vorbehandlungstemperatur in Cl_2 auf der Abszisse. Die Kurve ist die Mittelwertkurve aus 10 Messungen. Die Kurve ist die Mittelwertkurve aus 10 Messungen.

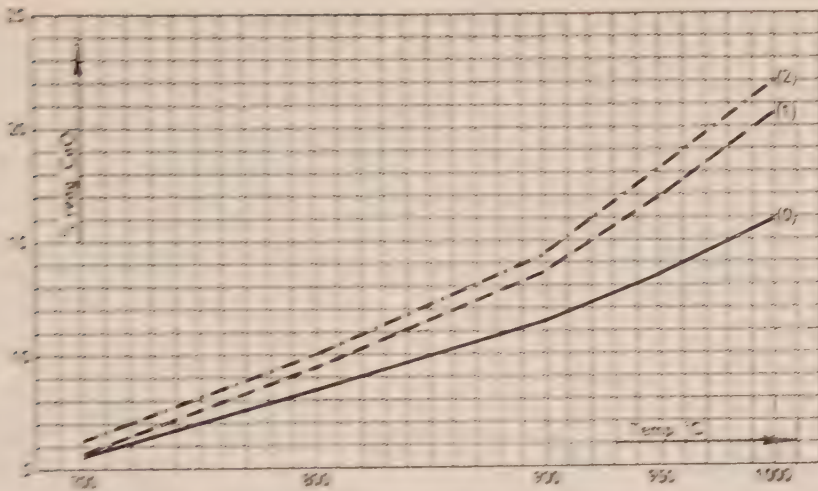


Abb. 4. Quarz, $O_2(N_2)$ vorbehandelt bei 600° (1) und 900° (2) — Luft (3).

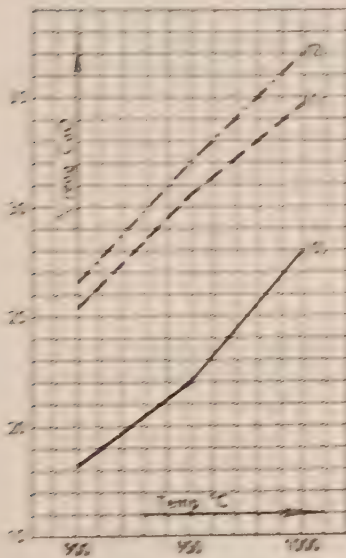


Abb. 5. Trypsin, $O_2(N_2)$ vorbehandelt bei 600° (1) und 900° (2) — Luft (3).

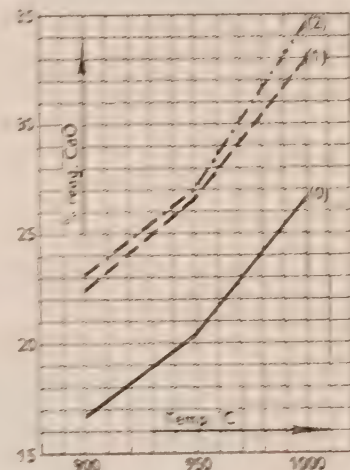


Abb. 6. Cristobalit, $O_2(N_2)$ vorbehandelt bei 600° (1) und 900° (2) — Luft (3).

denen, die man an Kristallinität oder Amorphosität aufweist. Es versteht sich von selbst, dass diese Befunde auch im Interessengebiet der Pneumatik liegen.

Die vorstehende und auch technisch sehr wichtige Interesse besitzen einige von uns zum Teil früher veröffentlichte Untersuchungen von unter gegebenen Umständen chemisch behandelten Gases auf die Kristallinität oder amorphisierten Kristallinität. Diese Untersuchungen sind — je nach der Diffusionsgeschwindigkeit

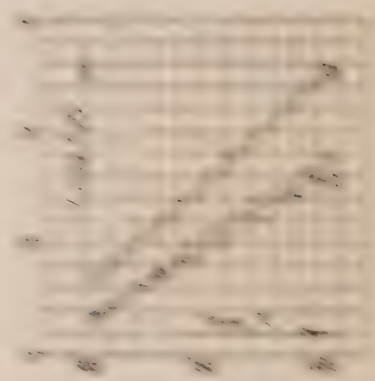
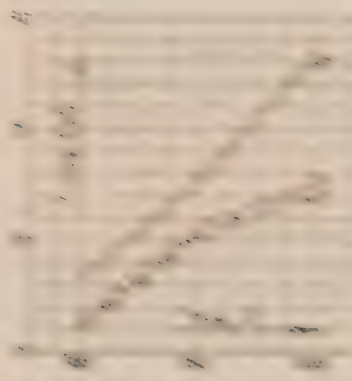
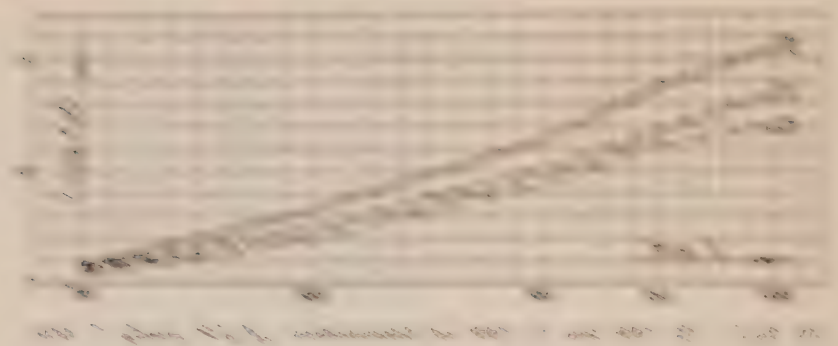


Abb. 1. Verlauf der Temperatur während der Zeit.

Abb. 2. Verlauf der Temperatur während der Zeit.

Die Temperatur der Luft während der Zeit wird durch die Zeit bestimmt. Die Temperatur der Luft wird durch die Zeit bestimmt.

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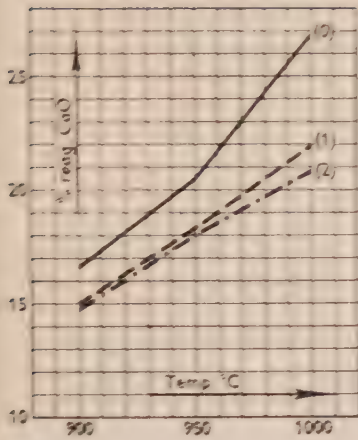


Abb. 10.

Abb. 10. Cristobalit, $\text{SO}_2(\text{N}_2)$ vorbehandelt bei 600° (1) und 900° (2) — Luft (0).

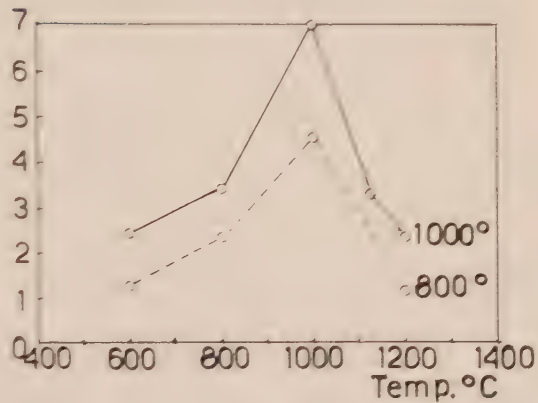


Abb. 11.

Abb. 11. Die Figur zeigt (Ordinate) die Differenz in % Umsetzung (CaO - Quarz) zwischen in O_2 und in N_2 vorbehandelten SO_2 Präparaten bei verschiedenen Vorbehandlungstemperaturen (Abszisse) und bei der beiden Reaktionstemperaturen 800 und 1000° . Man sieht, dass die durch Vorbehandlung erzeugte Abweichung bei der Umwandlung von Quarz in Cristobalit ein Maximum hat.

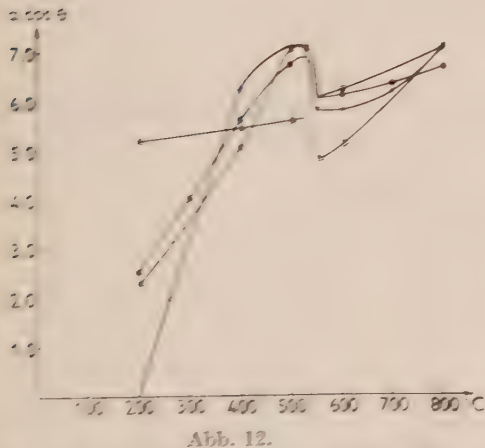


Abb. 12.

Abb. 12. Becherglaschen nach Vorbehandlung der Quarzpräparate in N_2 3 Stdn. (—) : 5 Stdn. (●) : Vakuum 1 Stde. bei 800° , dann in O_2 2 Stdn. und im Exsiccator 1 Stde. (○) : Vakuum 1 Stde. bei 800° , dann in O_2 2 Stdn. und Exsiccator 1 Woche (□) : Die Einwirkung des Treibmittels verläuft im Glas der unvorbehandelten Anzeiger. Vorbehandlungstemp.

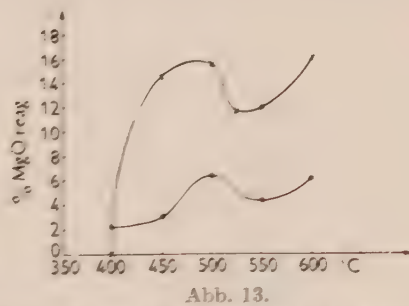


Abb. 13.

Abb. 13. Umsetzung zwischen MgO (400) und Kingglas, entwässert in Vakuum 3 Stdn. bei 600° (○). MgO (1000) und Kingglas, entwässert in Vakuum 3 Stdn. bei 600° (●).

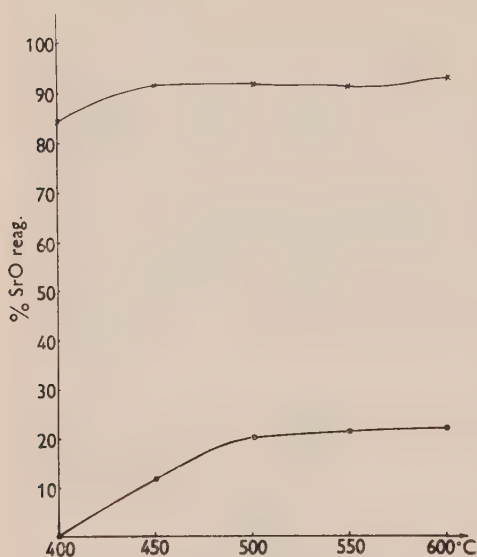


Abb. 14. Umsetzung zwischen SrO und Sr-Na-Glas, entwässert im Vakuum 3 Stdn. bei 550° (●); „bewässert“ im Autoklav 2 Stdn. (×).

usw. bedeutet, dass die vorbehandelten Präparate (nach der Vorbehandlung) bei Zimmertemperatur mit N_2 „gewaschen“ wurden um ev. Adsorptionsschichten von Vorbehandlungsgasen zu entfernen.

Es war zu erwarten, dass kristallographische Umwandlungsvorgänge sich auch bemerkbar machen sollten. Die Abb. 11 zeigt dies sehr deutlich.

In gewissen Fällen lässt sich ein solcher Einfluss auch im Transformationsintervall von Glassorten nachweisen, Benetzungsversuche mit Kapillaren aus Jena-Supremaxglas (Abb. 12) und Reaktionsversuche mit MgO und Kronglas sind als Beispiele gewählt. (Abb. 13). MgO wurde aus $MgCO_3$ hergestellt, teils bei 400°, teils bei 1000°.

Ein selbstverständliches Interesse für die pneumatolytischen Vorgänge und dabei vorkommende amorphe Substanzen, wie z. B. Obsidian, besitzen einige Versuche über die Reaktionsfähigkeit von verschiedenen Glassorten im feuchten und

Tabelle 1. Diopsid ($CaO \cdot MgO \cdot 2 SiO_2$).

Erhitzungsbedingungen	Temp. °C.	Röntgendiagr.
Luftstrom: 0,2 Atm. H_2O	1 000	CaO , MgO
Druck: 1 Atm.	1 100	CaO , MgO
Druck: 1 Atm.	1 200	Diopsid, Cristobalit
	1 300	Diopsid
Luftstrom: 0,7 Atm. H_2O	900	CaO , MgO
Druck: 1 Atm.	1 000	Diopsid, Cristobalit
Druck: 1 Atm.	1 100	Diopsid, Cristobalit
Druck: 1 Atm.	1 200	Diopsid
Autoklav: Luft plus H_2O	400	$CaCO_3$, MgO
Druck: 300 Atm.		
Autoklav: Luft plus H_2O	520	Diopsid
Druck: 500 Atm.		

Tabelle 2. Andradit ($3 \text{ CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3 \text{ SiO}_2$).

(Erhitzungsbedingungen: Autoklav, Luft plus Wasserdampf.)

Temp. °C.	Zeit in Stdn.	Druck	Andradit (+) oder nicht (-) gebildet
400	65	300 Atm.	—
520	68	500 Atm.	+
550	65	180 Atm.	+
700	64	200 Atm.	—

im trockenen Zustand mit MgO und einigen Erdalkalioxyden. Von den Reaktionsversuchen mit Glas sei hier nur das System SrO–Sr–Na–Glas genannt. Man sieht was für eine grosse — allerdings hier recht komplizierte und noch unvollständig untersuchte — Rolle der Wassergehalt spielt (Abb. 14).

Vor einigen Jahren führten R. Jagitsch und Verfasser eine Reihe Untersuchungen über die Mineralbildung durch Pulverumsetzungen bei verschiedenen Temperatur- und Druckverhältnissen aus. Diese Experimente umfassten viele Mineralien z. B. Diopsid und Andradit.

Aus pneumatolytischen Gründen wurden vergleichende Untersuchungen im Autoklav mit oder ohne Anwesenheit von Wasserdampf ausgeführt.

Die Tabellen 1 und 2 zeigen, teils dass reine Pulversynthesen wie zu erwarten auch in solchen Fällen möglich und druckabhängig sind, teils auch, dass der Wasserdampf eine Rolle spielt auch wenn die Mineralien kein Kristallwasser enthalten.

Tryckt den 12 december 1960

Uppsala 1960. Almqvist & Wiksells Boktryckeri AB

Perite, a new oxyhalide mineral from Långban, Sweden

By MARIANNE GILLBERG

With a chemical analysis by ALEXANDER PARWEL

ABSTRACT

Perite, PbBiO_2Cl , a new oxyhalide mineral occurs as a sulfur-yellow fissure mineral in a manganese skarn from Långban, Sweden. The density is 8.16 g cm^{-3} , hardness about 3, refraction probably > 2.4 . An X-ray investigation shows that perite is orthorhombic pseudotetragonal. The space group is $Bmmb$ (D_{2h}^{17}) and the cell dimensions $a = 5.627 \pm 0.050 \text{ Å}$, $b = 5.575 \pm 0.020 \text{ Å}$, $c = 12.425 \pm 0.090 \text{ Å}$. A synthetic perite has also been prepared with $a = 5.593 \pm 0.002 \text{ Å}$, $b = 5.558 \pm 0.002 \text{ Å}$, $c = 12.428 \pm 0.008 \text{ Å}$. The unit cell contains 4 formula units, and its volume is 391 Å^3 . The structure type is the same as for nadorite, PbSbO_2Cl . Atomic parameters: $z_{\text{Pb}} = 0.385$, $z_{\text{Bi}} = 0.090$, $z_{\text{Cl}} = 0.75$. The atomic distances are: Pb-4 O 2.45 Å , Pb-4 Cl 3.30 and 3.25 Å , Bi-4 O 2.27 Å , Bi-4 Cl 3.45 and 3.42 Å .

Introduction

Several lead, arsenic and antimony-bearing oxyhalide minerals have been found at Långban, Sweden. Minerals belonging to this group are: mendipite, ecdemite-heliophyllite, nadorite, blixite and to a certain extent, sahlinite.

In 1940 the late Professor Aminoff found that a mineral having the appearance of ecdemite contained bismuth. The mineral has been registered by Flink (1923) as number R13 in his list. Four specimens containing that mineral have been found in the Långban collection preserved at the Department of Mineralogy, Swedish Museum of Natural History. In this paper I intend to describe this lead-bismuth-oxyhalide mineral and name it in honour of Professor Per Geijer (born 1886), the well-known Swedish economic geologist and petrologist. According to the usual nomenclatural principles, the mineral ought to be named geijerite. However, there is already a mineral called geyerite (in German geierit) from the locality Geyer in Saxony (Breithaupt, 1866). The similarity between Geyer and Geijer makes the use of surname unsuitable and for that reason I propose to use the Christian name of Professor Geijer and call the mineral in question perite. This usage is similar to torbernite after Torbern Bergman.

The material used for this investigation was collected in the drift of Råmen (130-metre level) where mining began in the year 1894.

Table 1. Chemical analysis of natural perite.

Analyst: A. Parwel.

	Weight %	Impurities subtracted and re- calculated to 100 %	No. of mol. per unit cell	No. of cations per unit cell	No. of anions per unit cell
H ₂ O < 110°	0.04				
Insoluble residue	1.00				
H ₂ O > 110°	0.10	0.10	0.11	0.22	0.11
PbCl ₂	26.33	27.47	1.90	1.90	3.80
PbO	23.69	24.71	2.13	2.13	2.13
Bi ₂ O ₃	45.74	47.72	1.97	3.94	5.91
MnO	0.46				
CaO	1.44				
MgO	0.07				
CO ₂	1.19				
	100.06	100.00	6.11	8.19	11.95

Physical and optical properties

Perite is a sulfur-yellow mineral with yellow streak and adamantine luster. It does not fluoresce in either long or short wave-length ultraviolet radiation. Its hardness on the Mohs scale is about 3 and the density was found to be 8.16 g cm⁻³. The mineral is easily soluble in dilute mineral acids. The habit of perite is commonly tabular with a relatively distinct cleavage perpendicular to the *c*-axis. The refraction of perite has not been determined, because it is too high for usual immersion liquids and reacts with melts of mixed sulfur and selenium. It is, however, probable that the index of refraction is greater than that of nadorite (2.40 *n_v*), since bismuth has higher atomic refractivity than antimony. Accordingly, the index of refraction of perite is probably greater than 2.4.

Occurrence

Perite occurs as an extremely rare fissure mineral. The size of the plates is about 0.5 mm and these form aggregates in a manganese skarn consisting essentially of hausmannite, calcite, and a black mineral probably belonging to the ludwigite-vonsenite group, and a few very small crystals of a red, not yet identified mineral.

Chemical composition

About 700 mg perite was hand-picked from specimen RMA g 1051 for the chemical analysis. It was, however, very difficult to avoid small amounts of impurities. These are 1.44 % CaO and 0.07 % MgO, being equivalent with 1.19 % CO₂, forming 2.70 % calcite (cf. Table 1). The manganese content probably derives from hausmannite, which also belongs to the mineral association. A qualitative spectrochemical analysis also showed traces of Fe and Al. The density was de-

terminated to be $8.00 \pm 0.01 \text{ g cm}^{-3}$. Corrections for the calcite and manganese content gave the value of 8.16 g cm^{-3} for perite. The volume of the unit cell calculated from the cell lengths is 391 \AA^3 (see page 567). On the basis of the density the "molecular weight" of the unit cell is found to be 1922. The values in columns 3-5 of Table 1 have been calculated using this figure. The formula of the specimen analyzed is $\text{Pb}_{4.03}\text{Bi}_{3.94}\text{O}_{7.93}\text{Cl}_{3.80}(\text{OH})_{0.22}$. The number of metal atoms is 7.97, which within the limit of error is equal to 8, corresponding to the number of atoms of oxygen. The bound water content ($> 110^\circ\text{C}$) is interpreted to be present as hydroxyl ions. The number of chloride and hydroxyl ions is equal to 4.02. Consequently, the unit cell contains 4 formula units of PbBiO_2Cl . This formula is analogous to nadorite, PbSbO_2Cl .

Synthesis

Perite was synthesized by fusing together PbCl_2 , PbO and Bi_2O_3 in proportions corresponding to the formula PbBiO_2Cl , except for a surplus of PbCl_2 . The mixture was fused in a porcelain crucible and the resulting product was cooled very slowly. The excess of PbCl_2 was removed by prolonged leaching with cool distilled water. A Guinier powder photograph of the material showed that it was almost identical with natural perite. Slight differences in the unit cell dimensions are probably due to impurities in the natural perite.

Unit cell and space group

Separate crystals of perite with developed faces do not occur in the present material, so that morphological determinations could not be carried out.

The X-ray investigation is essentially based on powder methods. For determining the unit cell a Guinier powder photograph ($\text{Cu}_{K\alpha_1} = 1.54051 \text{ \AA}$) was taken (cf. Table 2). To simplify indexing, an equatorial Weissenberg photograph was taken with the rotation axis perpendicular to the best cleavage in order to locate the supposed c -axis. The following dimensions of the unit cell were found:

$$a = 5.627 \pm 0.050 \text{ \AA} \quad b = 5.575 \pm 0.020 \text{ \AA} \quad c = 12.425 \pm 0.090 \text{ \AA}.$$

For synthetic perite the corresponding values are:

$$a = 5.593 \pm 0.002 \text{ \AA} \quad b = 5.558 \pm 0.002 \text{ \AA} \quad c = 12.428 \pm 0.008 \text{ \AA}.$$

These values are about the same as those found for nadorite (Sillén and Melander, 1941). They found:

$$\text{For natural nadorite} \quad a = 5.59 \text{ \AA} \quad b = 5.43 \text{ \AA} \quad c = 12.20 \text{ \AA}.$$

$$\text{For synthetic nadorite} \quad a = 5.58 \text{ \AA} \quad b = 5.43 \text{ \AA} \quad c = 12.21 \text{ \AA}.$$

The number of indexed reflections was small (cf. Table 2). As in nadorite the following classes of reflections were possible.

Table 2. Powder photographs of perite. *a*, lines used for determining the unit cell of natural perite. *b*, lines used for determining the unit cell of synthetic perite.Guinier camera. $\text{CuK}\alpha = 1.54051 \text{ \AA}$, cut-off 20 \AA .

<i>a</i> $\sin^2 \theta$ obs	<i>b</i>		<i>I</i> (1-10)	<i>h k l</i>
	$\sin^2 \theta$ obs	$\sin^2 \theta$ calc		
.0153	.0153	.0153	2.5	002
.0419	.0418	.0418	8.5	111
.0615	.0614	.0613	3	004
.0727	.0725	.0726	10	113
	.0758	.0758	7.5	200
.0762		.0762	} double.	020
	.0912	.0912		202
.1382	.1382	.1382	4 broad	006
.1521	.1520	.1520	5	220
	.1674	.1674	1.5 broad	222
.1945	.1944	.1943	3.5	131
.2146	.2145	.2144	4 double? broad	026
.2250	.2299	.2250	7	133
	.2902	.2903	2	226
	.3033	.3034	} double	400
.3045	.3046	.3048		040
.3654	.3654	.3651	2	404
	.3794	.3796	2	420

$$\begin{array}{ll}
 h k l & (h+l)=2n \\
 0 k l & l=2n \\
 h 0 l & (h+l)=2n \\
 h k 0 & h=2n; k=2n \\
 h 0 0 & h=2n \\
 0 k 0 & k=2n \\
 0 0 l & l=2n
 \end{array}$$

This is in agreement with the conditions of space group No. 63 *Bmmb* (D_{2h}^{17}).

Powder data

In order to simplify identification of the mineral from other localities some powder photographs were taken with a Philips 114.83 mm camera using Ni-filtered Cu radiation ($\lambda = 1.5418 \text{ \AA}$). The results are given in Table 3, and are similar to those of nadorite. The strongest lines for natural perite are: 3.77 \AA (8); 2.86 \AA (10); 1.620 \AA (9) and 1.251 \AA (8).

Atomic arrangement

The similarity in space group and unit cell dimensions between nadorite and perite naturally suggested that they belong to the same structure type. The

Table 3. Powder photographs of perite. *a*, natural perite. *b*, synthetic perite.

CuK α radiation, $\lambda = 1.5418$ Å. Philips 114.83 mm camera.

d_a	d_b	I	$h\ k\ l$
6.18	6.19	5	0 0 2
3.77	3.77	8	1 1 1
3.08	3.08	6	0 0 4
2.86	2.87	10	1 1 3
2.78	2.77	7	2 0 0, 0 2 0
2.07	2.07	7	0 0 6
1.970	1.969	7	2 2 0
1.881	1.881	2	2 2 2
1.745	1.745	6	1 3 1 (3 1 1)
1.660	1.660	7	0 2 6 (2 0 6)
1.620	1.618	9	1 3 3 (3 1 3)
1.427	1.427	6	2 2 6
1.394	1.395	6	4 0 0, 0 4 0
1.301	1.300	5	1 1 9, 3 3 1
1.273	1.274	3	4 0 4 (0 4 4)
1.251	1.248	8	4 2 0 (2 4 0)
1.158	1.157	7	4 2 4 (2 4 4)

atomic parameters had to be determined from the Guinier powder photograph. In analogy with Sillén and Melander (*op. cit.*) the following atomic positions can be expected:

$$(0, 0, 0; \frac{1}{2}, 0, \frac{1}{2}) +$$

$$4\text{ Pb}; 4\text{ Bi and }4\text{ Cl in }4\text{ (c) }0, \frac{1}{4}, z; 0, \frac{3}{4}, \bar{z}$$

$$8\text{ O in }8\text{(e) }x00; \bar{x}00; x\frac{1}{2}0; \bar{x}\frac{1}{2}0$$

Assuming that the anions occupy ideal positions: 4 Cl in $z=0.750$ and 8 O in $x=0.250$, the parameters of Pb and Bi were determined by trial and error.

The best agreement with the observed intensities was found with $z_{\text{Pb}}=0.385$ and $z_{\text{Bi}}=0.090$.

Nadorite		Perite	
x	z	x	z
Pb	$0.380 \pm .002$	Pb	0.385
Sb	$0.078 \pm .005$	Bi	0.090
Cl	$0.756 \pm .010$	Cl	0.75
O	$0.25 \pm .02$	O	0.25

Again, as in nadorite, the metal ions form double layers very similar to those in tetragonal X_1 compounds (Sillén, 1940), in which each double metal layer contains a sheet of oxygen atoms. The metal-oxygen layers are separated by single sheets of Cl ions. In conformity with nadorite, the lead atoms have moved from the oxygen in the direction of halogen sheets. The following atomic distances have been found:

M. GILLBERG, *Perite, a new oxyhalide mineral from Långban, Sweden*

Nadorite (Sillén and Melander 1941)

Perite

Pb-4 O 2.44 Å

Pb-4 Cl 3.18 Å

Sb-4 O 2.17 Å

Sb-4 Cl 3.39 and 3.54 Å

Pb-4 O 2.45 Å

Pb-4 Cl 3.30 and 3.25 Å

Bi-4 O 2.27 Å

Bi-4 Cl 3.45 and 3.42 Å

ACKNOWLEDGEMENTS

The writer wishes to express her gratitude to Prof. F. E. Wickman, Swedish Museum of Natural History, for his kind interest and help, and to Mr A. Parwel for the chemical analysis.

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Magnussonite from Sterling Hill, New Jersey

By CLIFFORD FRONDEL

During a visit to the Naturhistoriska Riksmuseet in 1950, the writer was shown a specimen of the new mineral just described by Gabrielson¹ under the name magnussonite. This mineral was recognized as similar to an undescribed manganese arsenite from Sterling Hill, New Jersey, that has lain dormant in the Harvard collection since 1931 for lack of sufficient material for a satisfactory investigation. With the aid of a specimen of magnussonite supplied by Dr. Frans Wickman and an advance copy of the description by Dr. Gabrielson, it has proved possible to establish the complete identity of the two minerals.

The Sterling Hill material is green in color, with a vitreous luster. It occurs as a fine-grained crust in a slickensided veinlet that cuts the massive franklinite-zincite-willemite-calcite ore. Only about 100 mg of the mineral are preserved. The X-ray powder pattern is indistinguishable from that of the Långban material. Under the microscope the mineral is isotropic with $n_O = 1.983 \pm .005$. The specific gravity of a pure but small sample (10 mg) was measured on a microbalance as $4.14 \pm .05$. A chemical analysis of the mineral, made in 1934 by L. H. Bauer (deceased) on a very small sample, is cited below. There is

CaO	MgO	FeO	MnO	ZnO	SiO ₂	As ₂ O ₅	SiO ₂	Cl	H ₂ O +	Total
0.84	0.74	1.35	45.82	2.17	1.40	47.42	1.40	nil	0.58	100.32

some uncertainty as to the way the analysis was handled. The arsenic was reported as As₂O₅, but definitely is present in the trivalent state. The original specimen label also titles the mineral as an arsenite, and the analysis sheet adds that the SiO₂, ZnO, FeO, MgO and CaO "probably are mostly present as foreign attachments or inclusions". In any case, the analysis is sufficient to confirm the identity of the mineral with magnussonite from Långban.

Harvard University, Cambridge, Massachusetts.

¹ Gabrielson, O.: Arkiv för min., this issue.

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